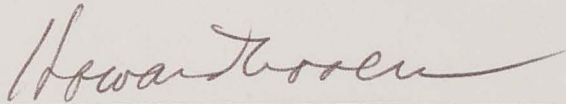


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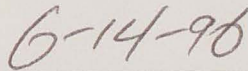
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Howard D. Mooers, Ph.D.

A handwritten date "6-14-96" in dark ink, written over a horizontal line.

Date

GRADUATE SCHOOL

DETERMINATION OF GROUNDWATER RECHARGE AND RESIDENCE TIME
IN THE ITASCA MORaine AREA, NORTH-CENTRAL MINNESOTA:
A HYDROGEOCHEMICAL APPROACH

A THESIS
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
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BY

SHARI ANN KANUIT

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MASTER OF SCIENCE

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ABSTRACT

The Itasca moraine, because of its size and relief, is suspected to influence the groundwater flow regime of north-central Minnesota by serving as a major recharge area driving regional flow. This study uses hydrogeochemistry to determine the spatial distribution of recharge and discharge areas in the context of previously-defined glacial landform assemblages. The chemical evolution of groundwater along a flowpath results in a difference in the chemistry of juvenile and evolved waters. The effects of topography on flow systems become apparent in the spatial analysis of juvenile and evolved chemistries. Topography influences the development of oxidizing zones and local flow systems which, in turn, affect the groundwater chemistry. The broad, flat outwash plain south of the moraine is found to be an area of high recharge, the hummocky stagnation complex an area of moderate recharge, and the low-lying, undulating till plain north of the moraine an area of discharge.

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The residents of Lake Itasca and the other communities in the study area also deserve mention. Thanks to the landowners who allowed me to sample their wells and to the patrons of the Headwaters Inn who advised me of many valuable sampling locations. The personnel of the Becker, Clearwater, and Hubbard counties Soil and Water Conservation District offices were instrumental in the location of well records. Thanks also to Char Franck for providing lodging for my lesser field assistant, Bo.

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INTRODUCTION

The Itasca moraine is an east-west trending ice stagnation complex in north-central Minnesota, a massive accumulation of glacially-deposited sediments with a local relief of up to 200 meters. The moraine is approximately 130 km in length and 30-60 km in width (Figure 1). Because of its relatively high topographic relief and broad geographic extent, this landform is thought to be a source of recharge for the regional groundwater flow system (Siegel, 1983). The hydrologic influence of the moraine is speculated to extend to the Rainy River along the northern border of Minnesota (Siegel, 1983).

In an investigation that encompassed an area of approximately 1700 km² (twelve 7.5-minute USGS topographic quadrangle maps, Figure 2), St. George (1994) used inverse numerical modeling to evaluate the spatial distribution of recharge in the Itasca moraine area. Landforms were defined on the basis of relief, stratigraphy, sedimentology, and glaciogenic origin. They were then grouped into assemblages. These landform assemblages served as fundamental hydrostratigraphic units, each with characteristic aquifer parameters. Hydraulic conductivities were specified based on field data and laboratory analyses. After application of appropriate boundary conditions, a numerical model was run and calibrated by varying recharge uniformly over each landform assemblage.

The current study seeks to test the recharge model of St. George (1994) using a hydrogeochemical approach. The chemical compositions of groundwater from wells within the moraine and from wells in adjacent non-moraine areas display differences indicative of dissimilar residence times. Recently recharged waters have chemistries similar to precipitation; they are dilute and oxidized. Groundwater in discharge areas has had more time to react with aquifer materials. Its chemical composition is attributable to both reactions with aquifer materials and to the reducing conditions encountered deeper in

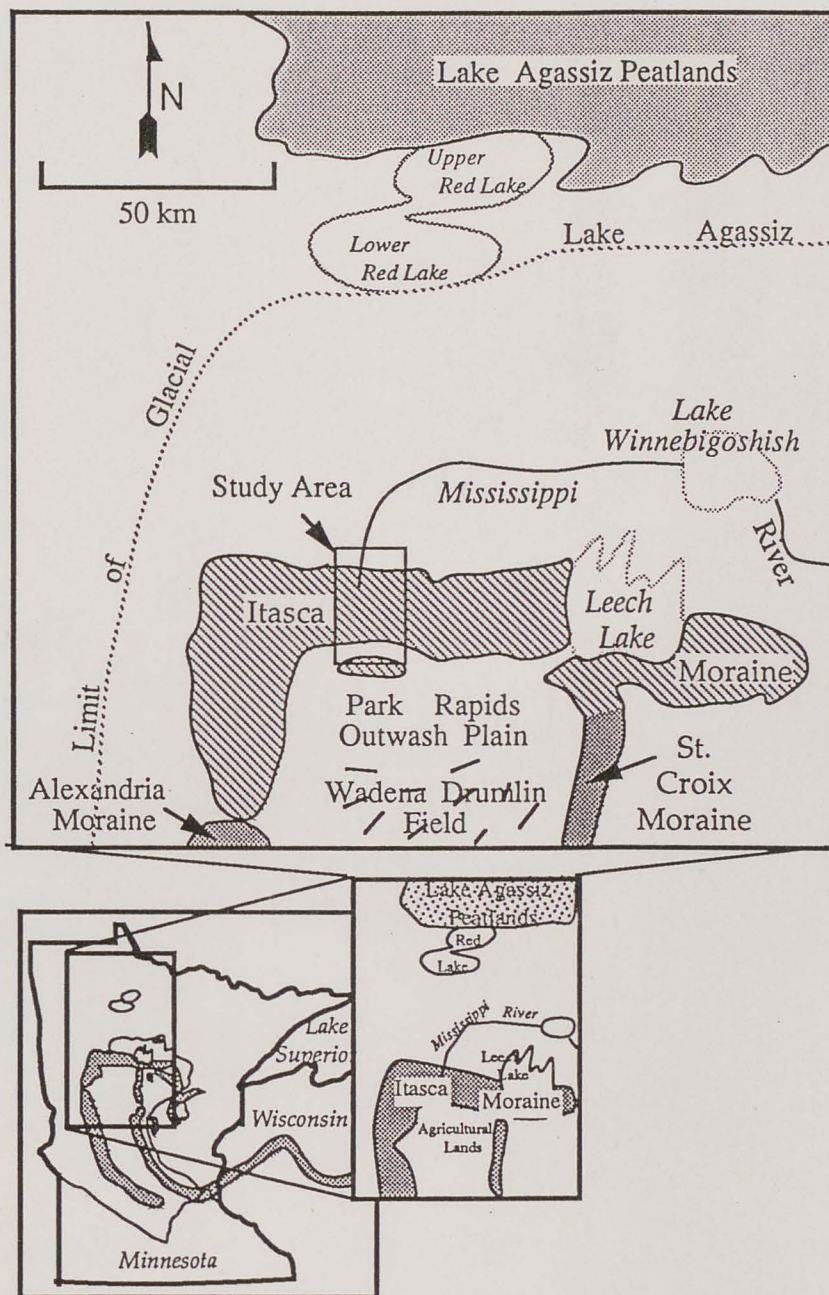


Figure 1. Glacial landscape of north-central Minnesota including the Itasca moraine (from Mooers, unpublished).

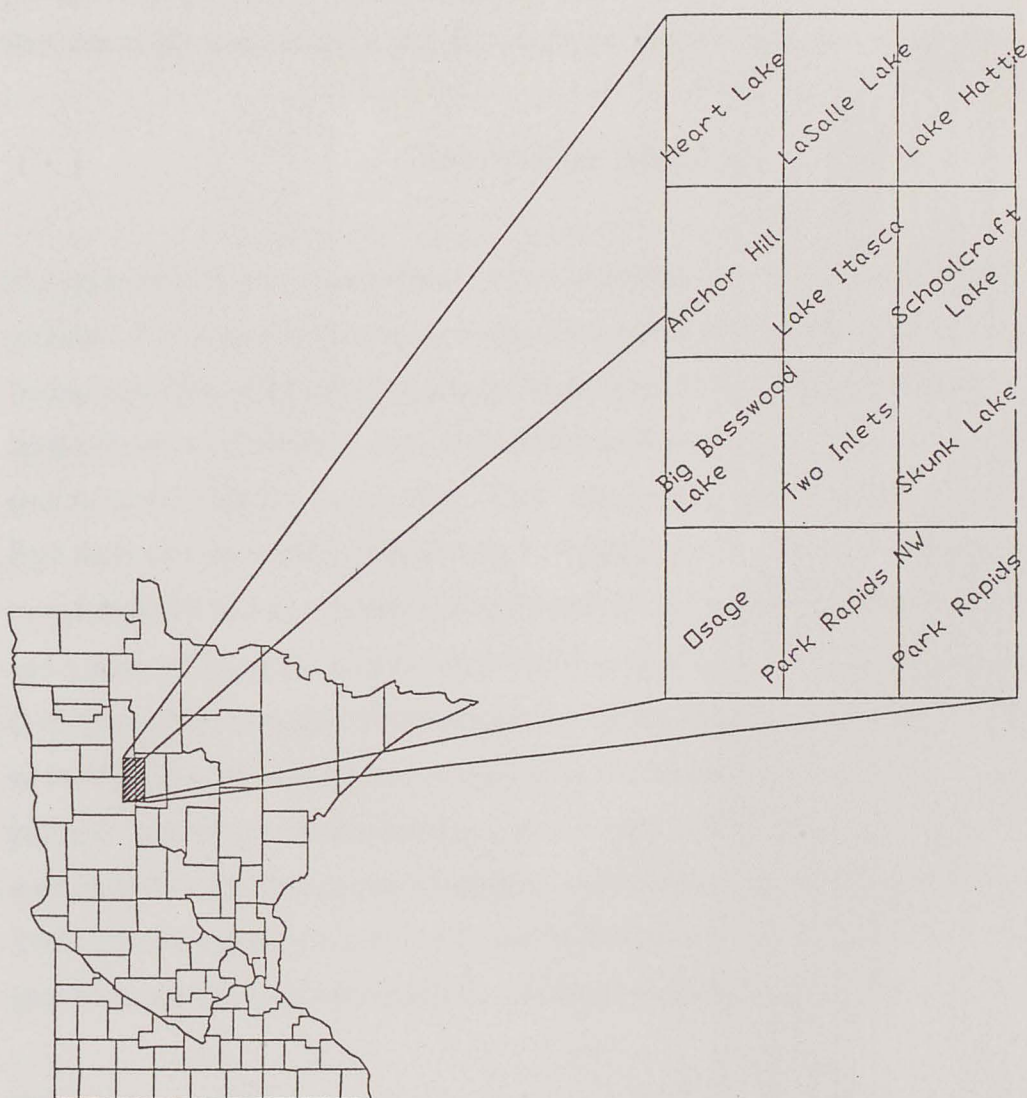


Figure 2. The study area and the 7.5-minute quadrangles it comprises (modified from St. George, 1994).

the surficial aquifers. Isotopic age-dating also distinguishes older discharge waters from younger recharge waters. The agreement between results of the chemical and physical elements of this study demonstrates the validity of the methods employed by each.

THE STUDY AREA

The study area (Figure 2) lies within portions of Becker, Clearwater, and Hubbard counties. Park Rapids is the largest residential area with a 1980 population of 2,772. Itasca State Park, which encompasses the headwaters of the Mississippi River, is in the northern portion of the study area. The climate is characterized as humid continental with cool summers (*Goode's World Atlas*, 1990). Mean annual precipitation at Itasca State Park during the years 1951-1980 was 66.6 cm (Megard et al., 1993). Mean annual temperature for the same period was 3.0 °C with a mean summer temperature of 17.9 °C and a mean winter temperature of -13.9 °C (Megard et al., 1993). Oakes and Bidwell (1968) calculated an annual evapotranspiration for the Mississippi Headwaters watershed of 19.98 inches (50.75 cm) based on eighty years of climatological records. The land is primarily used for agriculture, forestry, and recreation. Agricultural lands in the southern portion of the study area produce hay, small-grain crops, corn, and potatoes (Stark et al., 1991). Forested areas are both conifer and hardwood and include second- and third-growth stands harvested for paper pulp and wood products (Stark et al., 1994).

GEOLOGY

Early investigations of the glacial history of Minnesota were undertaken by N.H. Winchell, the first Minnesota state geologist, and his assistant, Warren Upham, through the years 1872 to 1895. In 1906 Frank Leverett, assisted by Frederick B. Sardeson, began field work which would eventually lead to his completion of maps and descriptions of Minnesota's glacial geology (Leverett and Sardeson, 1919; Leverett, 1929, 1932). In

more recent times, the glacial geology of northwestern Minnesota has been revised and elaborated upon by Wright (Wright and Ruhe, 1965; Wright, 1972), Harris (1975), Sackreiter (1975), Anderson (1976), Perkins (1977), Hobbs and Goebel (1982), Norton (1982), Mooers (1988), Goldstein (1989), and Meyer (1993).

The landscape of the Itasca moraine area is quite heterogeneous. The moraine itself is topographically high and hummocky, its extent delimited by the random, crowded distribution of small lakes and hills typical of a glacial stagnation complex (Flint, 1971; Sugden and John, 1976). To the north is a till plain with fewer lakes and much more subdued relief. Both of these features are dissected by tunnel valleys, many accommodating lakes (Wright, 1993). Extending southward from the Itasca moraine is the broad, flat Park Rapids outwash plain (Norton, 1983). The outwash sediment covers the northern portion of the Wadena drumlin field, and the drumlins emerge from the gravel cover just south of the study area (Figure 1). All of these components of the regional landscape are a consequence of glacial activity during Wisconsin glacialation.

The vertical and areal distribution of drift and landforms in the area records the history of the advances and retreats of the Wadena lobe of the Laurentide ice sheet (Figure 3 illustrates the following sequence of glacial events). An exception to this is the pre-Wisconsinan age Browerville till which underlies drift derived from the Wadena lobe and originated from an ice advance from the northwest prior to the first advance of the Wadena lobe (Goldstein, 1989). The earliest advance of the Wadena lobe was thought to have reached beyond the Minnesota River Valley (Wright, 1972). However, Gowan (1993) cast severe doubt that the ice extended this far.

The most well-defined ice margin of the Wadena lobe is the Alexandria moraine, which marks the terminus during the Hewitt phase of Late Wisconsin glacialation (Wright, 1972; Goldstein, 1985). The moraine was deposited during a standstill of the ice terminus of

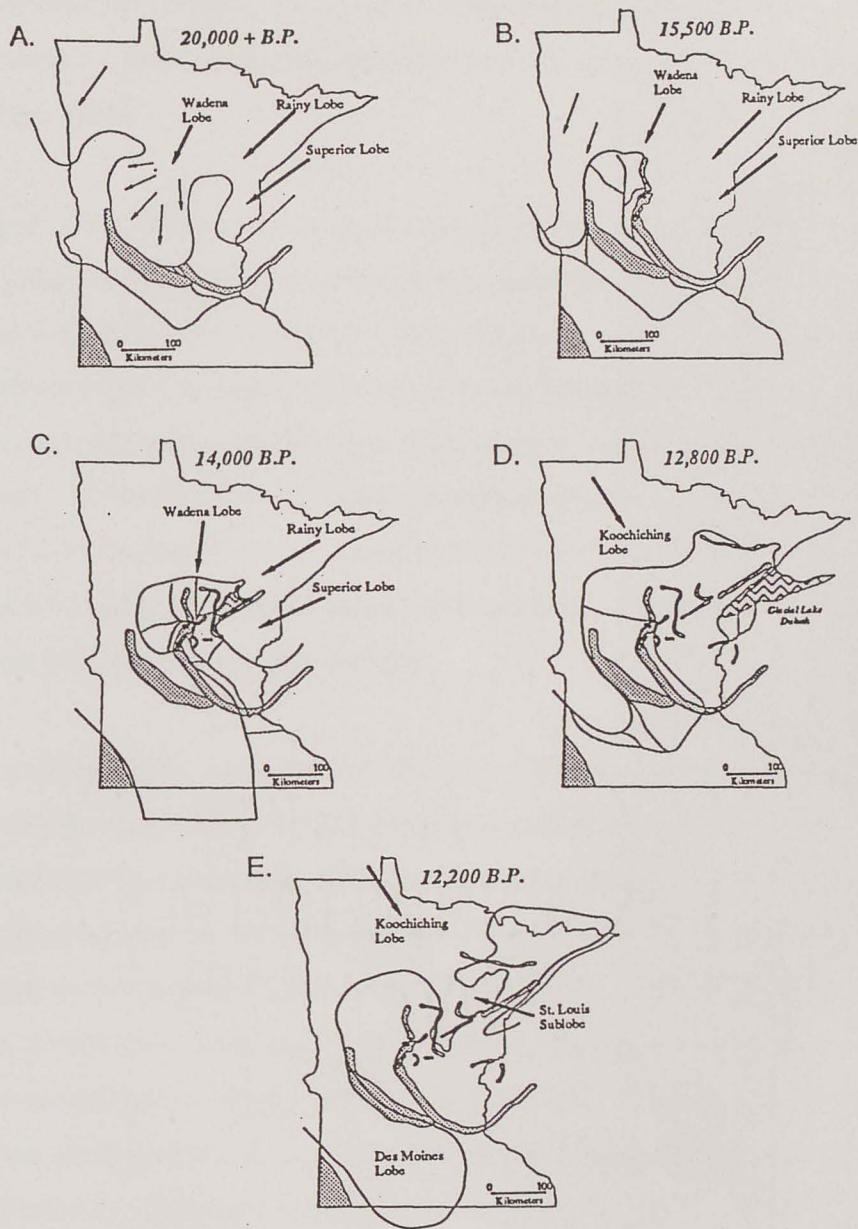


Figure 3. Glacial events responsible for the development of the landscape. A. Advance of the Wadena lobe to the Alexandria moraine during the Hewitt phase. B. Retreat and readvance of the Wadena lobe to the Itasca moraine during the Itasca/St. Croix phase. C. Retreat of the Rainy lobe, allowing a shift in the direction of ice flow to the southeast. D. The southeastward advance of the Koochiching lobe. E. Advance of the St. Louis sublobe (from Mooers, unpublished).

unknown duration (Wright, 1993). Deposition of the drumlin till and concurrent formation of the Wadena drumlins followed the formation of the Alexandria moraine (Goldstein, 1985).

The origin of the Wadena lobe in the Hewitt phase is subject to interpretation. Wright (1972, 1993) maintains that the carbonate content of the till indicates the Winnipeg lowland of southern Manitoba (northwest of the study area) is the source of the ice, and the southwestward orientation of the drumlins can be explained by diversion of flow from southeast to southwest, a consequence of blockage by an ice mass in northeastern Minnesota. Goldstein (1989) proposes a northeastern origin, suggesting the calcareous nature of the till is due to contamination from the underlying carbonate-rich till. In a study of the geochemistry of the tills, Gowan (1993) concluded that the Wadena lobe derived its carbonate from the Hudson Bay lowlands.

These conflicting interpretations notwithstanding, it is accepted that the Hewitt phase ended with the retreat of the Wadena lobe and eventual readvance from the north-northeast to the Itasca moraine. This was contemporaneous with the advance of the Rainy and Superior lobes to the St. Croix moraine (Wright, 1993). The advances are collectively designated as the Itasca/St. Croix phase (Wright, 1964). While the Wadena lobe held its position at what was becoming the Itasca moraine, meltwater under high hydrostatic pressure carved tunnel valleys 15-60 m deep in the drift. Obvious examples of tunnel valleys are those presently occupied by Lake Itasca and other lakes in the area (Wright, 1993) (Figure 4). Meltwater also left behind an extensive outwash plain south of the moraine complex.

Recent research indicates that instead of the retreat of the Wadena lobe being followed by the advance of the St. Louis sublobe, the retreat of the Rainy lobe allowed a change in direction of ice flow from the northwest while the Wadena lobe held its position at the

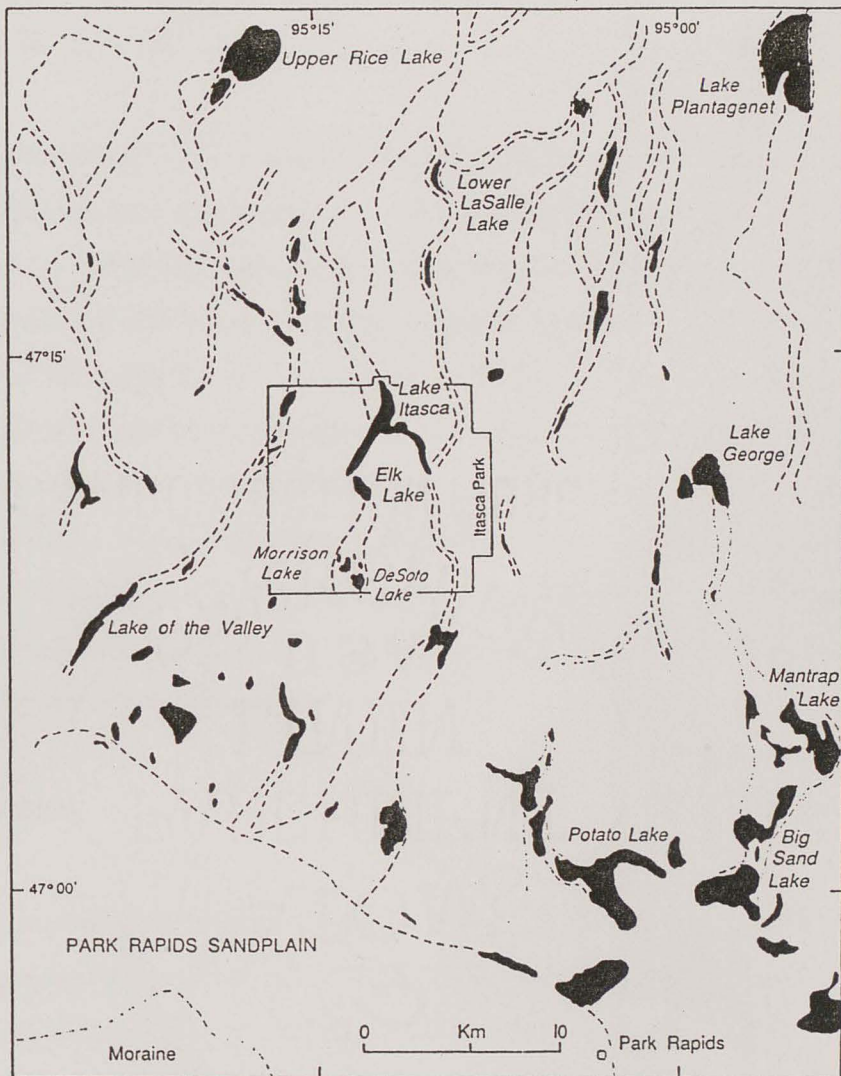


Figure 4. Tunnel valleys occupied by lakes in north-central Minnesota (from Wright, 1993).

Itasca moraine. The reoriented flow is referred to as the Koochiching lobe, as the lithological characteristics of the entrained debris differ from those of the drift deposited by the Wadena lobe. The Koochiching lobe was responsible for deposition of the uppermost till plain in the northern part of the study area (St. George, 1994; St. George and Mooers, in press).

Drift sedimentology is fundamental to the understanding of groundwater chemistry in glacial-drift aquifers. Goldstein (1985, 1989) studied the sedimentology of the Wadena drumlin field. From his results, the following inferences are drawn concerning the sedimentology of drift in the study area. The drift lithology is a product of the bedrock in the source area of the ice that deposited it. Drift derived from ice flowing from the northwest will likely contain fine-grained Paleozoic limestone and dolomite of the Winnipeg lowland and perhaps Cretaceous marine siliceous and calcareous shales of the Williston Basin. Drift of northeastern origin will consist of magnetite-rich, coarse-grained igneous and sedimentary rocks. Drift from ice originating to the north is identified by the presence of granite and greenstone. Incorporation of older drift into overriding ice can result in a mix of these lithologies.

HYDROLOGY

The surface- and groundwater hydrology of the region is influenced by the landscape's glacial genesis. Most of the area is covered with lakes, the most notable being the linear lakes occupying tunnel valleys primarily north of the moraine and the legion of small lakes within the hummocky topography of the moraine (Wright, 1993). There is also a tremendous amount of small wetlands in the moraine. The lakes and wetlands form in closed depressions surrounded by hills (Figure 5). The area south of the moraine is fairly devoid of surface water because of the sandy, easily-drained outwash sediments (Figure 6). The study area is drained by four major rivers: the Mississippi and Schoolcraft in the



Scale 1:24000

Figure 5. Lakes and wetlands within the hummocky stagnation complex.



Scale 1:24000

Figure 6. Outwash sediments lacking in surface water.

north and the Straight and Fishhook in the south (Figure 7). These rivers are hydraulically connected to the drift aquifers that are the focus of this study.

The surficial aquifer as defined by St. George (1994) includes the deposits overlying the Hewitt till. The thickness of the unconfined drift aquifer ranges from less than 100 feet in the southern part of the study area to greater than 500 feet in the moraine. The sediments of the aquifer material range from sandy loam and loam tills to clayey lacustrine deposits to sands and gravels. Hydraulic conductivity varies according to landform: 10^{-6} to 10^{-4} cm/s in the till plains, 10^{-6} to 10^{-1} cm/s in the stagnation complex, and 10^{-4} to 10^0 cm/s in the outwash deposits (St. George, 1994).

The investigation by St. George (1994) suggests that groundwater in the study area flows from high-recharge areas within the moraine toward the Mississippi, Schoolcraft, Straight, and Fishhook rivers. In addition to baseflow lost to major rivers, groundwater is discharged in areas marked by springs and flowing artesian wells. The springs are located primarily north of the moraine, although there are sporadic springs within the hummocky stagnation complex and collapsed outwash landform assemblages of the moraine. Flowing wells to the northwest of the study area discharge large volumes of water (Figure 8).

Fluctuations in the water table occur seasonally with changes in vegetation and precipitation. Recharge to the aquifer occurs primarily in the spring, following snowmelt. There is usually not enough snow to recharge the groundwater; the water derived from melting snow wets the unsaturated zone, priming it for infiltration by spring rainwater, which recharges the groundwater. In late spring and summer, transpiration by vegetation depletes much of the soil moisture, precluding appreciable recharge. A decrease in plant growth and significant precipitation in the fall result in a second period of infiltration and recharge. The water table declines in the winter as precipitation is in the form of snow and the ground is frozen (D.O. Rosenberry, pers. comm.).

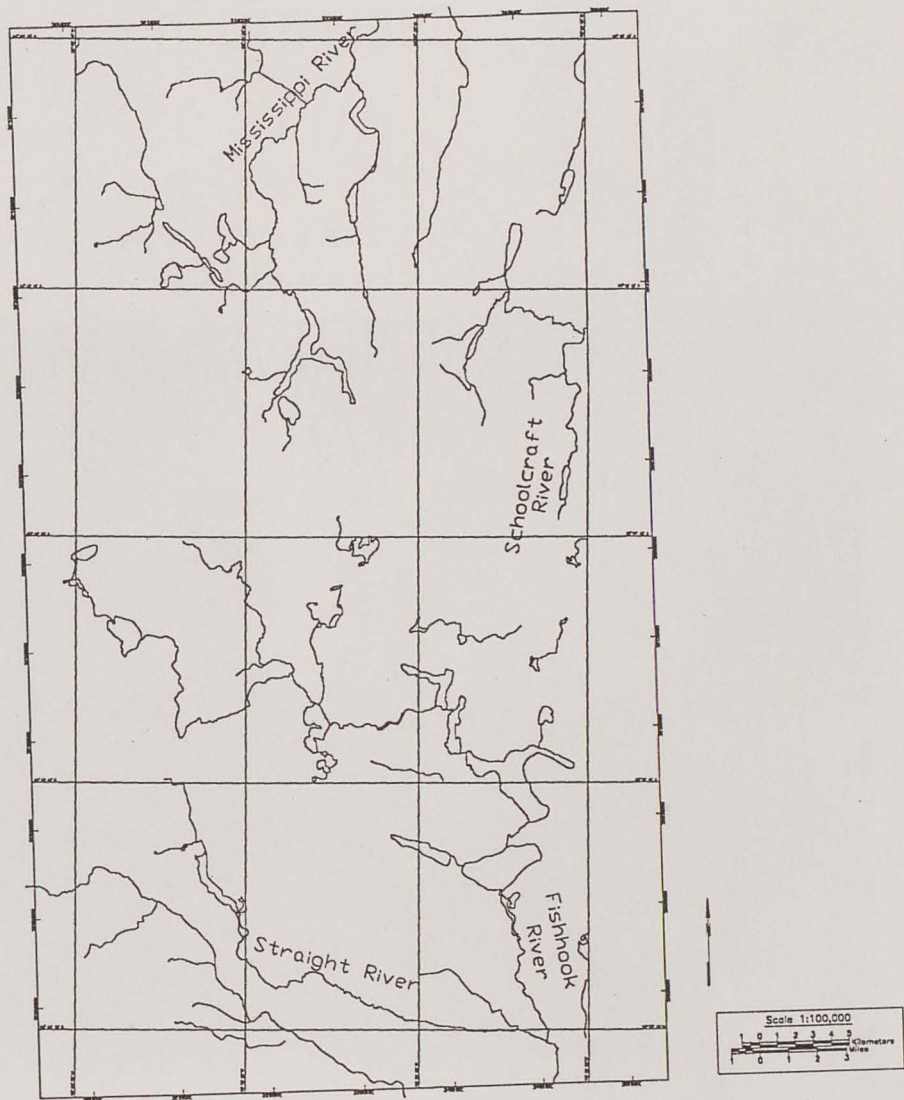


Figure 7. Major rivers in the study area (modified from St. George, 1994).



Figure 8. Flowing well near Nay-Tah-Waush, Minnesota, northwest of the study area.

PREVIOUS HYDROGEOLOGIC STUDIES

Several investigations have been undertaken that describe the hydrogeologic setting and groundwater resources in this part of Minnesota. The hydrology of the Mississippi headwaters area was summarized by Oakes and Bidwell (1968) in a regional-scale investigation. Their investigation involved the characterization of surface water and groundwater resources of the watershed and the compilation of data including precipitation, evapotranspiration, flow direction, stream discharge, and water quality. Groundwater availability and use were also inventoried as part of the study. Stark et al. (1991) similarly assessed the unconfined drift aquifers in the Bemidji-Bagley area, north of the study area. Groundwater resources--flow direction, water quality, and potential yield of the glacial drift aquifers--were the focus of this study. The aquifers defined were both the unconfined drift as well as the uppermost confined drift aquifers. There were insufficient data on aquifers underlying these to define or describe them adequately.

A more detailed local study in Hubbard county east of the study area investigates surface/groundwater interactions of Williams Lake and Shingobee River. This study is an ongoing project of the USGS involving the collection of climatic and hydrologic data by which the relationships between the two are characterized (Winter and Averett, in press).

The Straight River watershed, which lies in part within the southwest portion of the study area, was the focus of a recent study. Stark et al. (1994) evaluated the quantity and quality of both the surface water and groundwater, described the interaction between the river and the aquifer, and discussed the effects of irrigation on the ground- and surface water. Withdrawals for irrigation are of particular importance in the Straight River because it is a trout stream, and the corresponding decrease in groundwater discharge to the river tends to increase water temperature, thereby threatening the habitat of trout.

St. George (1994) used a landform-based approach to the estimation of recharge over the Itasca moraine. This study was the first to actually evaluate the role of the moraine in the regional groundwater flow regime of north-central Minnesota. Using inverse numerical modeling of groundwater flow, recharge was estimated over the various landform assemblages in the Itasca moraine area.

Mooers and Schulte (1993) and St. George (1994) described the criteria by which landforms are delineated. Landforms in this area were developed by a particular set of glacial processes. Similar landforms are grouped into landform assemblages. A landform assemblage is defined as an area with similar topographic expression, sedimentology, and stratigraphy throughout. The sedimentology and structure may be complex, but the degree of complexity is similar throughout the landform assemblage. A landform assemblage can range from a narrow channel to an extensive outwash plain; size is not a limiting factor in its definition. Once characterized, the information from one landform assemblage can be applied to other occurrences of the same landform assemblage throughout an area. This provides a convenient framework for the description of hydrogeologic properties in terms of spatial distribution over the study area.

St. George (1994) identified eight landform assemblages: till plains of the Wadena and Koochiching lobes, stagnation complex, lacustrine sediment, outwash channel, collapsed outwash, outwash fan, and outwash plain (Figure 9). Hydraulic conductivity, calculated on the basis of grain size analyses, was assigned to each landform assemblage. The landform thickness was determined from well records. Boundary conditions for the model domain were constant head boundaries at major rivers and no-flow boundaries at groundwater divides and study area boundaries to which groundwater flow is parallel. With this information the groundwater flow regime was modeled using MODFLOW, a

LEGEND TO ACCOMPANY FIGURE 9

Landform Number	Landform
1	Till Plain (Wadena Lobe)
2	Till Plain (Koochiching Lobe)
3	Stagnation Complex
3a	Main Complex
3b	Anchor Hill I
3c	Anchor Hill II
3d	Smoky Hills
4	Lacustrine Sediment
5	Outwash Channel
6	Collapsed Outwash
7	Outwash Fan
8	Outwash Plain

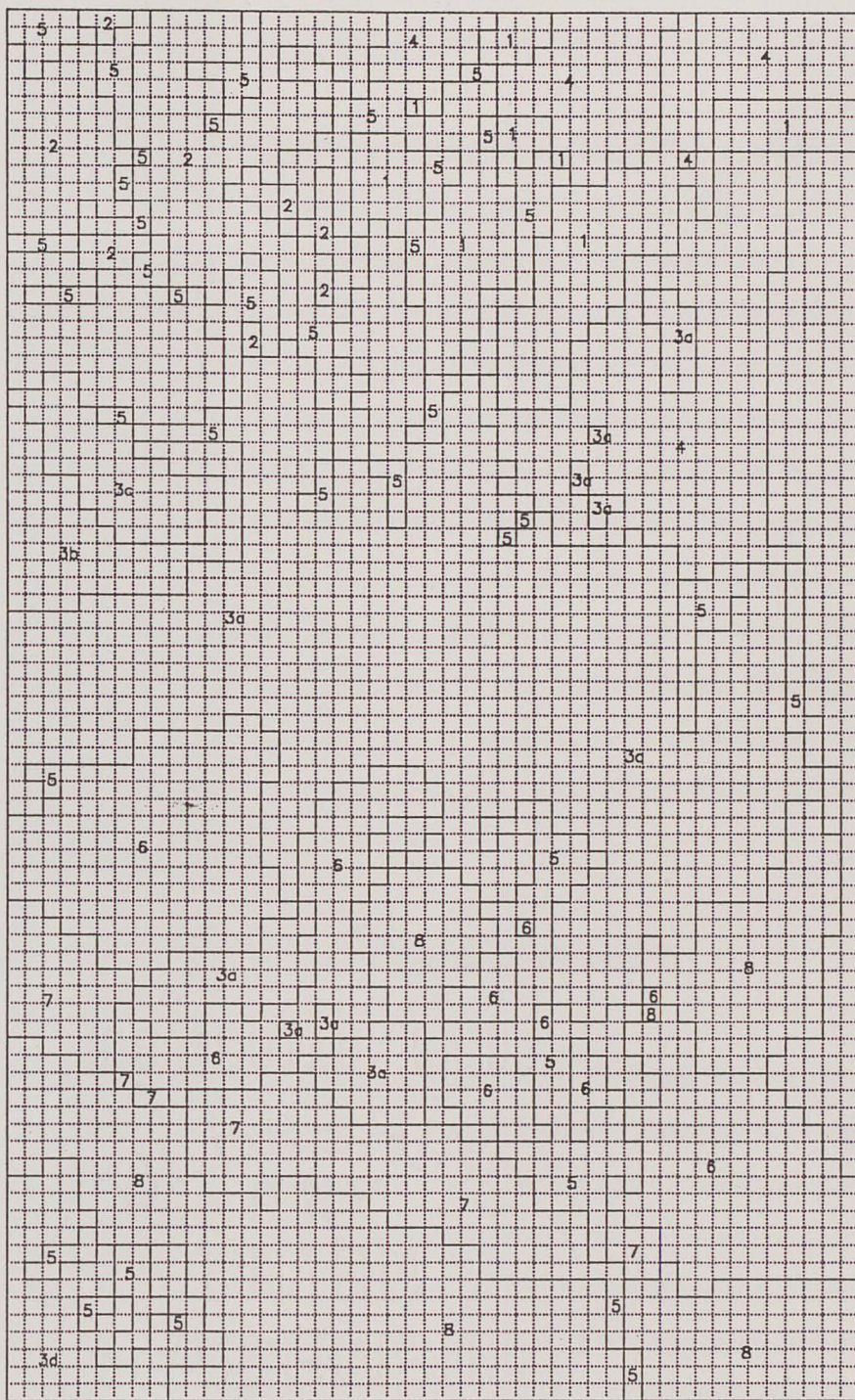


Figure 9. Landform assemblages identified by St. George (from St. George, 1994).

modular three-dimensional finite difference flow model developed by the USGS. Model calibration was achieved by varying recharge uniformly over each landform assemblage.

The results show considerable variation in recharge over the landform assemblages (St. George, 1994). The outwash plain south of the moraine is an area of high recharge. Hydraulic conductivity of the sandy sediments is high, and the topography is flat. These factors combine to effect a significant downward gradient to the groundwater flow. The collapsed outwash, although it also has high hydraulic conductivity, contributes less recharge to intermediate and regional flow systems than the outwash, a result of its hummocky topography. Much of the infiltration that occurs is lost to local depressions through short-residence-time local flow systems. This effect is even more pronounced in the stagnation complex as much recharge is lost to the many lakes and wetlands within the closed depressions. The stagnation complex is an area of moderate recharge. The till plain to the north is an area of discharge, or at least very little recharge. The till has low hydraulic conductivity, and the recharge from higher areas to the south drives groundwater flow to discharge in the lower-lying till plain. The results are shown on Figure 10.

OBJECTIVE AND HYPOTHESIS

The recharge parameter is integral to the development of hydrologic budgets of groundwater flow systems. An understanding of the hydrogeochemistry of groundwater can aid in the delineation of recharge areas. In this study, areas of recharge and discharge are identified based on their hydrogeochemical characteristics. Local and regional flow systems are distinguished by comparison of the chemical composition of the water as well as by age-dating and isotopic signatures. This information, in conjunction with modeling results from a previous study (St. George, 1994), enables the characterization of relative quantity of recharge within the omnigenous glacial sediments of the study area.

LEGEND TO ACCOMPANY FIGURE 10

Landform Number	Landform	Recharge (cm/yr)
1	Till Plain (Wadena Lobe)	0.15
2	Till Plain (Koochiching Lobe)	0.15
3	Stagnation Complex	
3a	Main Complex	1.2
3b	Anchor Hill I	-4.6
3c	Anchor Hill II	20.7
3d	Smoky Hills	8.5
4	Lacustrine Sediment	-0.15
5	Outwash Channel	6.1
6	Collapsed Outwash	7.6
7	Outwash Fan	15.2
8	Outwash Plain	21.3

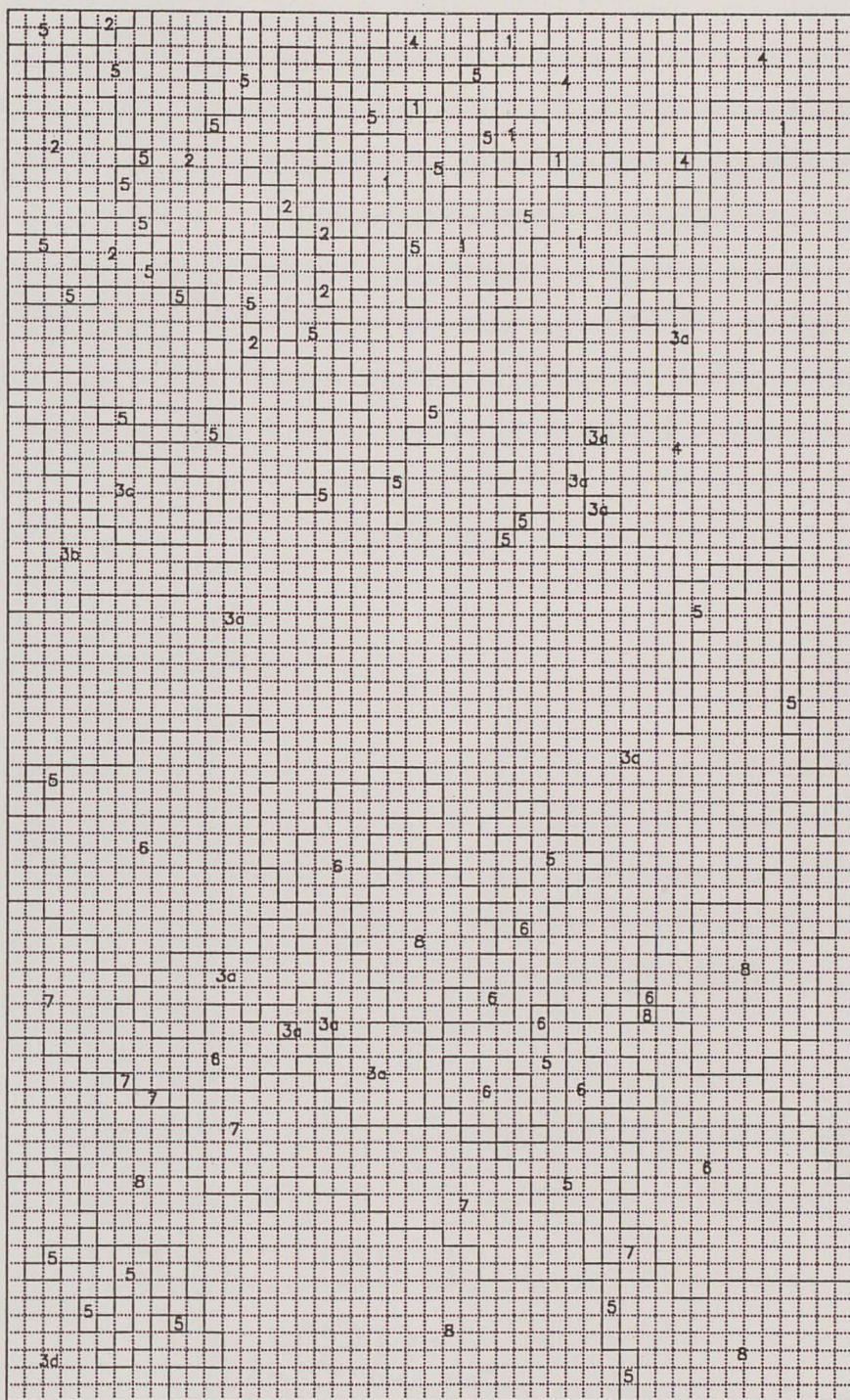


Figure 10. Recharge rates over the landform assemblages (from St. George, 1994).

It is expected that water in areas of recharge will have a different chemistry than water in areas of discharge. It is further expected that an evolution of the groundwater chemistry will be observed as the water first infiltrates the soil zone and unsaturated zone, reaches the water table, and then flows through the saturated zone to its point of discharge. Changes in chemistry within the saturated zone between the beginning and end of the flowpath may be subtle if the flowpath is short, precluding equilibration between the water and the aquifer material. The chemical signatures of recharge and discharge waters should, however, be sufficiently dissimilar to allow for distinction between the two.

METHODS

FIELD AND LABORATORY METHODS

Field work was conducted from June 3 to August 18, 1994. A total of 116 sites were sampled during this time: 89 wells, 14 surface water locations, and 13 springs or flowing wells. Six additional sites were visited but not sampled. Five of these were springs, the sources of which could not be found or were too difficult to reach for sampling. The other was a flowing well that was inconveniently flowing through a pipe propped up against a pine tree to a height of about five meters.

The field and laboratory methods employed in the collection and analysis of these samples follow the procedures prescribed by APHA (1989) or Alexander and Alexander (1992).

SAMPLE SITE SELECTION

The objective in the development of the sampling plan was to cover the areal extent of the study area as uniformly as possible and at a variety of depths and to effectively sample

each landform assemblage delineated by St. George. Domestic and public wells were selected for sampling from the Minnesota County Well Index (CWI), a database of well logs compiled by the Minnesota Geological Survey, and from well logs on file at Becker, Clearwater, and Hubbard counties Soil and Water Conservation District offices. The uniformity of the sampling network was limited by the sparse population in the area and by the inability to contact many landowners to obtain permission to sample their wells. Occasionally it was necessary to resort to the door-to-door approach. Well logs were not available for some sites, although landowners were able to provide at least the approximate well depth. Sampled springs were located by word of mouth and sheer luck, as were several flowing wells in and around the study area. Surface water samples were collected from the Mississippi, Schoolcraft, and Straight rivers at intervals dictated by bridges or landings for access. The sampling network is shown on Figure 11.

SAMPLE COLLECTION

Samples from wells were collected in a white (to minimize warming), five-gallon plastic bucket. Before collection of the sample the bucket was rinsed three times with sample water. Electrical conductivity was monitored while the sample was being collected to ensure stability of the well. That is, water collected was being drawn from the aquifer and had not been sitting stagnantly in the well. Of course, this was not cause for concern with flowing wells, but conductivity measurements were still taken. Upon collection of an acceptable sample, pH was the next measurement taken, followed by redox potential. Temperature was monitored throughout this process. Subsamples were collected from the bucket for analysis of alkalinity and major cations and anions. Sample bottles were labeled with a site number, name, and the type of sample the bottle contained. The site numbers begin with LI (Lake Itasca--home base) and continue with four numbers representing the month and year sampling took place. The last numbers, which range from 01 to 126, were assigned to each site in the order they were initially visited. An "R" at the end of a site

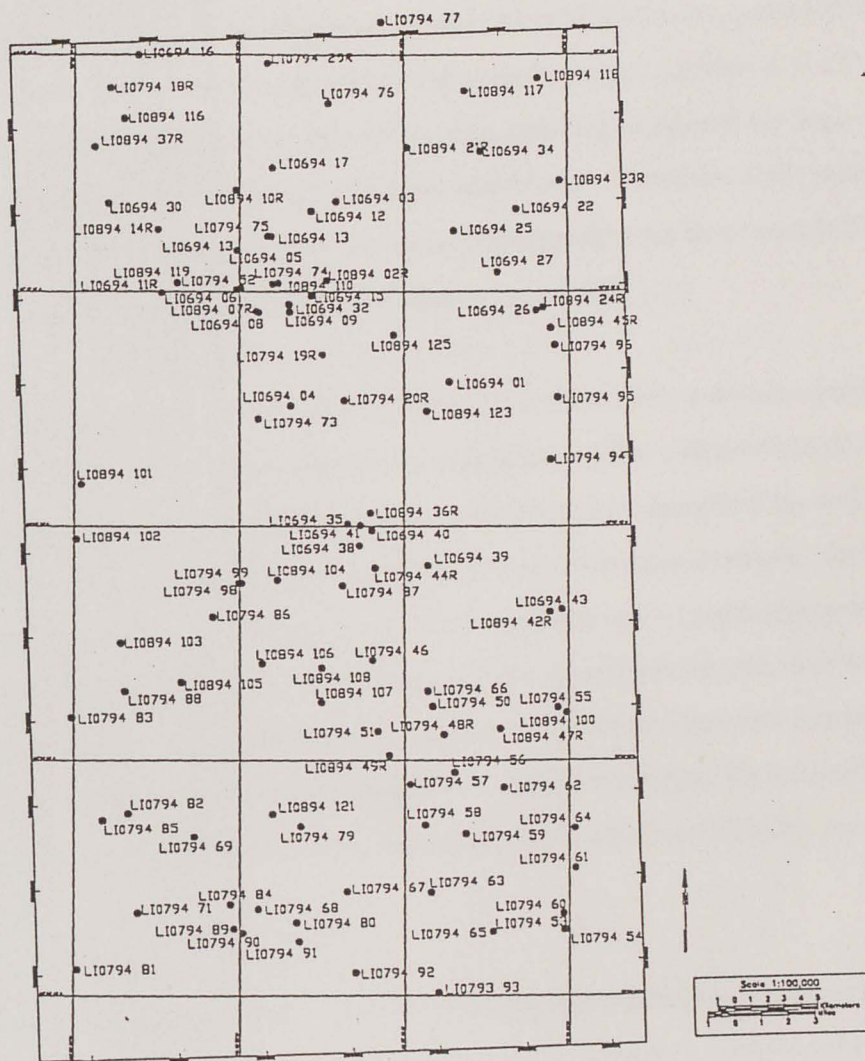


Figure 11. Groundwater sampling network (modified from St. George, 1994).

number indicates a repeat visit. The site name is the name of the landowner or the name of the spring, river, or closely associated body of water.

Although it is preferable to take all measurements and collect all subsamples from one large sample, this was not feasible for dissolved oxygen samples. Interaction with the atmosphere contaminated the samples with oxygen, resulting in excessively high D.O. levels not representative of actual groundwater conditions. Therefore, D.O. samples were not collected from the bucket, but were collected shortly after the large sample by the method described below (see "Dissolved Oxygen," page 25).

Springs were usually sampled by pumping water with the aid of a peristaltic pump into the rinsed bucket from a location as close to the source as possible. Measurements were taken and subsamples collected following the same procedure described for wells. D.O. samples were pumped directly into sample bottles and allowed to overflow. Some springs did not require the sample to be pumped; they flowed through a length of pipe and were thus collected in the same manner as if from a spigot. Conductivity, pH, and redox potential were sometimes measured by immersing the probe or electrode directly in the spring, if the nature of the flow was conducive to such a technique. In these cases sample bottles for alkalinity and major cations and anions were rinsed and filled by pumping from the spring.

Surface water samples were taken simply by dipping the bucket into the stream and proceeding in the usual manner. Dissolved oxygen levels were not measured at surface water sites.

CONDUCTIVITY

Conductivity, or specific conductance, is a measure of the ability of a solution to conduct an electric current. It is directly proportional to ionic strength; as the concentration of ions in a solution increases, so does its conductivity. Conductivity increases with temperature by about 2% per degree Celsius in response to changes in the ionic composition and viscosity of the water. In this study conductivity was used primarily as a measure of well stability, and, as such, a stable reading was more significant than the accuracy of the value measured (S.C. Alexander, pers. comm.).

A Hanna Instruments model HI8733 portable conductivity meter was used for measuring conductivity in the field. The meter measures conductivity in milli- or microsiemens per centimeter and has ATC (automatic temperature compensation). ATC was not used in this study, as it was not necessary for determining well stability, and the meter seemed to operate better without it. The manufacturer's specifications claim an accuracy of $\pm 1\%$, which may be optimistic. Hem (1989) suggests a range of $\pm 2-5\%$ for nonspecific conductivity equipment. The meter was calibrated with a standard 12.88 mS/cm solution of 0.1 M KCl. The measurement was taken by immersing the probe in the sample and recording the value in mS/cm once a stable value was reached.

HYDROGEN ION ACTIVITY

Many equilibrium and nonequilibrium chemical reactions, such as the dissociation of water, produce or consume hydrogen ions. The concentration of hydrogen ions therefore provides valuable information on the chemical processes taking place in a solution.

Field measurements were taken with an Orion 250A portable pH meter and an Orion Triode pH electrode. pH 7.0 and pH 10.0 buffers were prepared fresh daily and

equilibrated to sample temperature before calibration of the meter. Upon successful calibration of the meter to the two buffers, the measurement was taken, and temperatures were recorded from both the pH meter and a non-mercury thermometer immersed in the sample.

REDOX POTENTIAL

The redox potential is an expression of the intensity of oxidizing or reducing conditions in the solution. A platinum electrode immersed in the solution will spur a transformation from reduced state to oxidized state, causing a current of electrons to pass through the electrode. The electrode potentials were measured in millivolts using the Orion 250A portable pH/redox meter.

DISSOLVED OXYGEN

As water is exposed to the atmosphere, dissolved oxygen equilibrates and becomes saturated. The interaction with oxygen continues as the water moves through the vadose zone, until it reaches the water table where it is no longer in contact with air. Presence or absence of D.O. in the groundwater provides clues to such things as the age of the water, the biological activity taking place in the aquifer, and the rate of flow. Water that has recently infiltrated or has infiltrated rapidly will typically have dissolved oxygen, which is subsequently consumed by oxidation processes (Freeze and Cherry, 1979).

Extreme care must be taken when measuring D.O. to avoid contamination with the atmosphere. Samples were collected in duplicate by inserting a piece of plastic tubing into the spigot or hydrant, running the other end to the bottom of a 300 mL BOD bottle, and allowing the bottle to overflow for at least one minute before capping. This collection procedure proved effective in eliminating interaction with atmospheric oxygen.

Samples were titrated by the Winkler method with an azide modification using premeasured reagents manufactured by the Hach Company. First, the contents of one each Manganous Sulfate and Alkaline Iodide-Azide powder pillows were added to the BOD bottle. The bottle was inverted, and the precipitate was allowed to settle. The inversion was then repeated to ensure that the sample and reagents had reacted completely. Next, the contents of one Sulfamic Acid powder pillow were added to the BOD bottle. After mixing by inversion once again, 200 mL of sample were measured and transferred to an Erlenmeyer flask. This solution was titrated with 0.2 N Sodium Thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) to a pale yellow color, at which point Starch Indicator Solution was added, changing the color to dark blue. Titration was continued to a colorless endpoint. The digits required for titration were read from a Hach digital titrator and multiplied by 0.01, resulting in a D.O. value in mg/L.

ALKALINITY

Alkalinity is the acid-neutralizing capacity of the water, primarily a result of the carbon-containing species in the water: H_2CO_3 , HCO_3^- , and CO_3^{2-} . At pH values of the waters in this study, virtually all of the alkalinity can be attributed to HCO_3^- . H_2CO_3 accounts for a small percentage of the dissolved carbonate species at low to neutral pH (Drever, 1988; Hem, 1989).

Alkalinity samples were collected in 500 mL plastic bottles that had been acid washed, triple rinsed with distilled water, and oven dried overnight. The bottle was rinsed three times with sample water, and the final sample was capped without air and transported on ice to the lab. Within 24 hours the samples were titrated. An aliquot of approximately 90-110 g was measured and transferred to an Erlenmeyer flask, whereupon it was titrated with 1.6 N sulfuric acid to a bromcresol green-methyl red colorimetric endpoint pH of 4.8.

The final result was then normalized to 100 g. Hach Co. reagents were used for this analysis.

MAJOR CATIONS

Samples for cation analysis were collected in 60 mL bottles that had been rinsed with 2 N HCl, triple rinsed with distilled water, oven dried overnight at 80°C, and finally rinsed with sample water three times. The samples were acidified with 6 N reagent-grade HCl and kept on ice during storage and transport to the lab.

A Spectraspan III direct current argon plasma / optical emission spectrophotometer (DCP-ES) was used for cation analysis. Cations analyzed include the following: calcium, magnesium, iron, manganese, potassium, silica, phosphorous, strontium, aluminum, sodium, and barium. Concentrations are in units of mg/L.

MAJOR ANIONS

Samples for anion analysis (Cl^- , SO_4^{2-} , and $\text{NO}_3\text{-N}$) were collected in 60 mL bottles that had been soaked in distilled water for one week, triple rinsed with distilled water, and oven dried overnight at 80 °C. The bottles were rinsed three times with sample water before collection. The final samples were filtered through a 0.45 micron Millipore filter and kept on ice during storage and transport to the lab. Analysis was done at the University of Minnesota, Natural Resources Research Institute in Duluth, Minnesota using Dionex 2000I/SP ion chromatography.

Samples for analysis of ^{18}O , ^2H , and ^3H were collected in one-liter bottles that had been washed with soap and water, thoroughly rinsed with distilled water, and oven dried overnight at 80 °C. Sample bottles were not rinsed with sample water before collection. The isotopes were analyzed by the Environmental Isotope Lab at the University of Waterloo, Waterloo, Ontario. Tritium samples were enriched to reduce counting errors and to lower the detection limit to 0.8 TU.

QUALITY ASSURANCE / QUALITY CONTROL

The primary check on internal consistency of analyses is the charge balance. The sums of major cations and anions as well as the percent difference between them are included in the appended data. Six of the wells sampled were softened, causing a large negative percent difference due to the non-linear relationship between radiation intensity and very high sodium concentrations during DCP-ES analysis. These data were discarded along with four other data sets in which the charge balance exceeded +/- 6%. The charge balance for most samples was less than 2% of the total dissolved species (Figure 12).

In addition to the charge balance, consistency was assured by analysis of duplicate and spiked samples, by replication of field and laboratory titrations, and by prudent use of equipment. Duplicate analyses were performed on eighteen percent of cation samples and nine percent of anion samples. Twelve percent of the cation samples were spiked with 2 ppm iron after the initial cation analysis and were then re-run. These analyses are included as Appendix B. Dissolved oxygen titrations were performed in duplicate, and alkalinity titrations were performed in triplicate. The pH/redox potential and conductivity meters were carefully maintained according to the manufacturers' directions and were calibrated regularly.

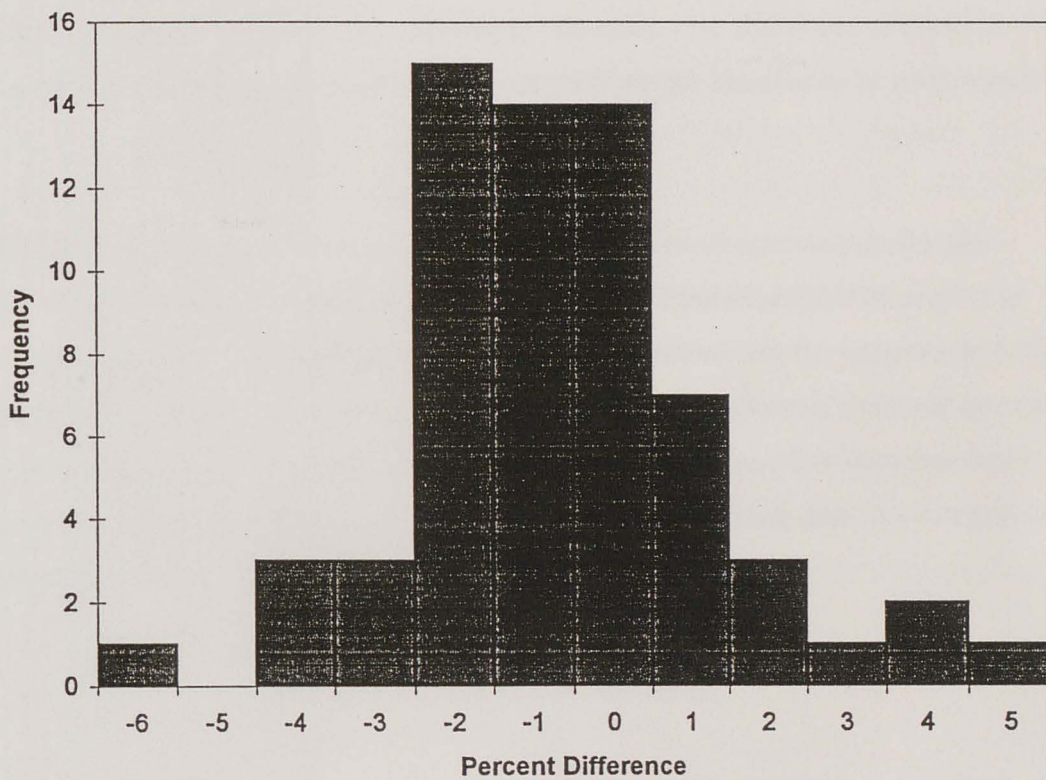


Figure 12. Histogram of calculated charge balances.

DATA INTERPRETATION

A conceptual model of the chemical evolution of groundwater from recharge to discharge was developed to serve as a basis for comparison with the data collected in this study.

The model is based solely on generalizations derived from the literature and is not specific to the landforms or lithologies encountered in this study. For this reason the data do not necessarily follow the predictions of this model; it is merely intended to be an interpretive guide.

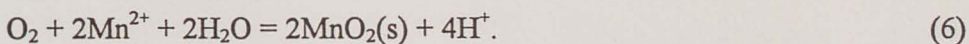
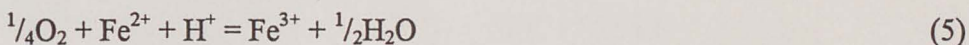
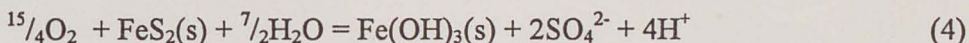
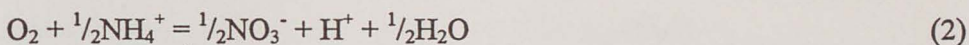
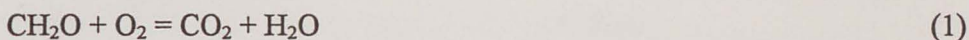
EQ3 (Wolery, 1992) was used to calculate the distribution of aqueous species, the activities of dissolved species, and the saturation state of the solutions with respect to numerous minerals. Chemical analysis of the water is entered into the program, including temperature, pH, redox potential, and the analytical concentrations of dissolved species. A thermodynamic database is employed in the generation of mass-law equations from which the distributions of species are calculated. This information aided the comparison of the different types of waters sampled.

CONCEPTUAL MODEL

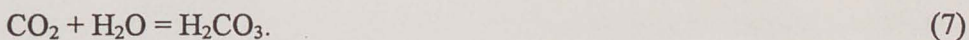
Understanding the geochemical evolution of groundwater along a flowpath is prerequisite to the differentiation of recharge and discharge areas. The change in chemistry as water matures from recharge to discharge is complex; it is dependent upon temperature, aquifer mineralogy, hydraulic properties of the aquifer, residence time, organic matter, and many other variables. Freeze and Cherry (1979) provide a concise explanation of the typical processes involved. Studies of chemical evolution in specific groundwater systems are documented by Rozkowski (1967), Palmer and Cherry (1984), Hendry and Schwartz

(1990), Weaver and Bahr (1991a and 1991b), Gerla (1992), Donovan and Rose (1994), and Cardenal et al. (1994).

As precipitation infiltrates the vadose zone it comes into contact with various biologic and geologic materials. In temperate climates the vadose zone contains soil horizons of diverse nature: the organic-rich "A" horizon, the "B" horizon, identified by accumulated clay and iron oxide, and the oxidizing "C" horizon (Freeze and Cherry, 1979). The chemistry of water entering the groundwater system as recharge and flowing through the vadose zone is heavily influenced by the presence of organic matter. Precipitation is generally dilute and oxidized. Dissolved oxygen (D.O.) content is very high, commonly 9 mg/L, because it is in contact with the atmosphere. Oxidation of organic matter (1), nitrification (2), and oxidation of hydrogen sulfide (3), iron sulfide (4), iron (5), and manganese (6) cause D.O. levels to drop rapidly upon infiltration according to reactions such as the following:



The CO_2 produced by the oxidation of organic matter and the water react to produce carbonic acid:



The carbonic acid moves downward through the soil by the processes of gas diffusion and aqueous transport. Its dissociation,

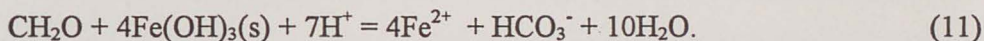


causes soluble salts from the upper soil horizons to dissolve and accumulate in the oxidizing zone. The dissolution of calcite by solutions rich in carbonic acid increases the alkalinity:

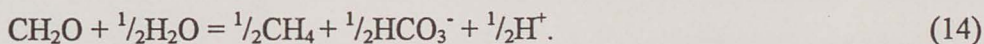
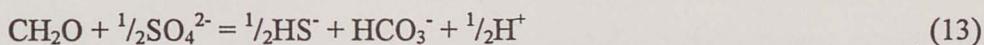
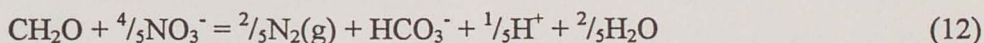


In summary, water that has infiltrated through the soil has the following characteristics in contrast to precipitation: lower, if any, D.O., higher dissolved solids, and higher alkalinity. The CO_2 content initially rises, but after becoming isolated from the atmosphere it steadily declines by consumption of carbonic acid in dissolution reactions, unless there is a source for replenishment of CO_2 such as methane fermentation or lignite coalification (Freeze and Cherry, 1979).

The consumption of D.O. by oxidation in the unsaturated zone results in reducing conditions. The reduction of Mn^{4+} (10) and Fe^{3+} (11) increases the concentration of Fe^{2+} and Mn^{2+} in solution:



Other reactions that may proceed in the reducing environment include denitrification (12), sulfate reduction (13), and methane fermentation (14):



As groundwater moves along a flowpath in the saturated zone, its chemistry evolves. Dominant anions along the flowpath evolve from bicarbonate in recharge areas to sulfate in zones of less active circulation to chloride in zones of sluggish flow and high total dissolved solids:

Travel along a flowpath \Rightarrow



Increasing age \Rightarrow

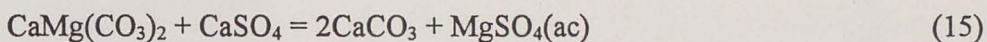
This is known as the Chebotarev sequence (Freeze and Cherry, 1979). There is no analogue for the evolution of dominant cations because of cation exchange. However, a few generalizations regarding the fate of cations in the saturated zone can be made. pH increases and Na^+ , K^+ , Mg^{2+} , and Ca^{2+} are released to solution as feldspars weather. The molal ratios Ca/Na and Mg/Na fluctuate in response to cation exchange on clay minerals, and Ca/Mg varies as a result of the incongruent dissolution of dolomite and dedolomitization. Clearly, the extent to which these processes affect groundwater chemistry is a function of aquifer mineralogy.

The carbonate system is a major factor in the chemical composition of many natural waters. Only a trivial amount of carbonate minerals in the aquifer is necessary for groundwater to reach saturation (Freeze and Cherry, 1979). Because the drift in the study area is calcareous, calcite and dolomite dissolution and precipitation presumably will have substantial influence on the groundwater chemistry.

Carbonate minerals are present in both the unsaturated and saturated zones. Dissolution of calcite and dolomite occurs under open system conditions in the unsaturated zone, because there is abundant CO_2 from root and bacteria respiration and oxidation of organic matter, and because groundwater in the unsaturated zone is, by definition, in contact with the atmosphere. When groundwater enters the saturated zone, a closed system, the CO_2 in the form of carbonic acid is consumed and alkalinity increases. Calcite dissolution is a more rapid reaction than dolomite dissolution, but given sufficient residence time both can reach saturation. Furthermore, calcite can become oversaturated as dolomite dissolves

and adds Ca^{2+} , CO_3^{2-} , and HCO_3^- to the system. Calcite must precipitate in order to maintain equilibrium. This phenomenon is the incongruent dissolution of dolomite.

If gypsum is encountered along the flowpath, which is not likely in this study area, dedolomitization may occur. As the gypsum is dissolved additional Ca^{2+} enters the system and, by the common ion effect, drives the calcite dissolution reaction to the left, resulting in calcite precipitation. At the same time dolomite continues to dissolve. The net reaction follows:



(Cardenal et al., 1994).

Dedolomitization and incongruent dissolution of dolomite affect Mg/Ca ratios, alkalinity, pH, and concentrations of ions in solution such as Ca^{2+} , Mg^{2+} , CO_3^{2-} , and SO_4^{2-} .

Stable isotopic composition is a means for identifying the source of groundwater. There are three stable isotopes of oxygen: ^{16}O , ^{17}O , and ^{18}O . ^{16}O accounts for 99.76% of the oxygen in water of the hydrologic cycle, and ^{17}O and ^{18}O account for 0.04 and 0.20%, respectively (Freeze and Cherry, 1979). Stable isotopes of hydrogen are ^1H and ^2H (or D for the name deuterium). Evaporation of seawater forms vapor depleted in the heavy isotopes ^2H and ^{18}O , because the vapor pressure of water containing heavy isotopes is less than that containing light isotopes. The isotopically light vapor subsequently condenses to rain, the heavy isotopes are preferentially condensed, and the vapor is further depleted in heavy isotopes. As the condensation continues north- and southward from the equator, landward from the ocean, and upward in elevation, the vapor continues to become more and more isotopically light. This process, called Rayleigh fractionation, is illustrated on Figure 13. A plot of $\delta^{18}\text{O}$ versus δD of precipitation (rain and snow) in various areas shows that these values are linearly related (as shown on Figure 20, page 50); they plot along the meteoric water line (Drever, 1988). If δD and $\delta^{18}\text{O}$ values for a

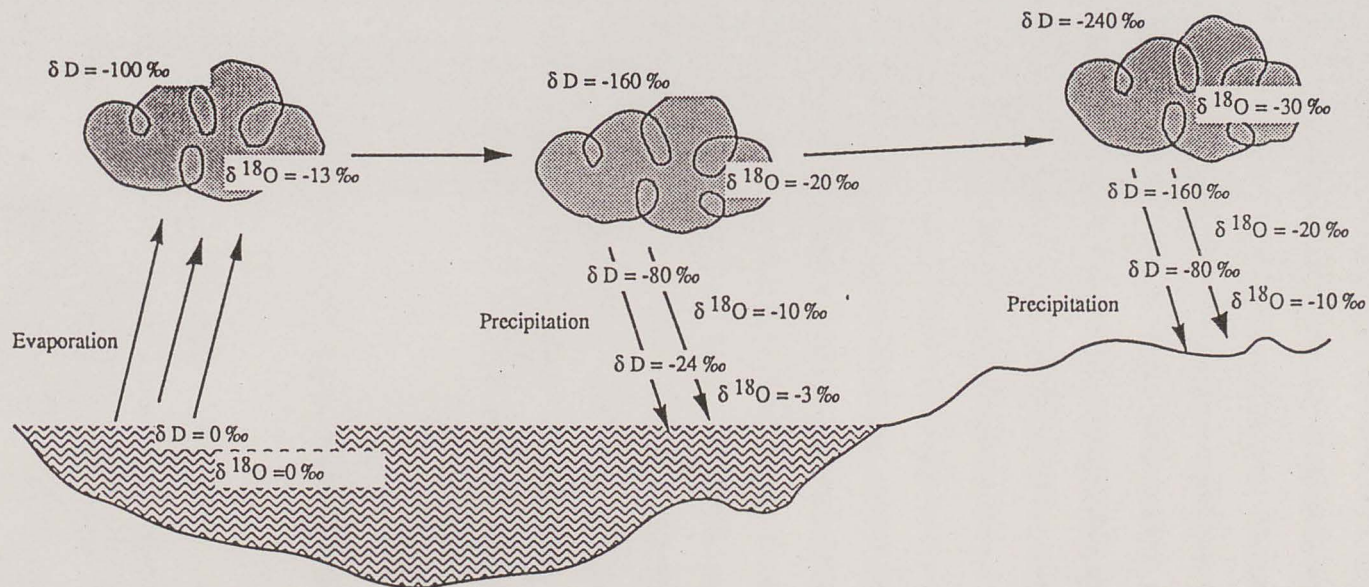


Figure 13. The process of Rayleigh fractionation and its effect on the stable isotopic composition of natural waters.

groundwater sample plot along this line, the water is most likely meteoric (Drever, 1988).

Tritium (^3H), a third isotope of hydrogen, can be used to age-date groundwater. Tritium is radioactive with a half-life of 12.3 years and is naturally occurring, produced by the interaction of cosmic rays with nitrogen and oxygen. Atmospheric levels of tritium prior to the year 1952 are estimated to be 5-20 tritium units (one tritium unit, or TU, equals 1 tritium atom in 10^{18} hydrogen atoms). From 1952 to 1969, testing of thermonuclear weapons released tritium to the atmosphere, raising levels above 1000 TU. Modern atmospheric levels are between 50 and 100 TU (Drever, 1988). The dearth of potentially contaminating hydrogen in geologic materials makes tritium an ideal groundwater age-dating technique. However, complications arising from the highly variable levels of atmospheric tritium over the past several decades, as well as possible mixing of waters of dissimilar age (Figure 14), somewhat limit its usefulness (Domenico and Schwartz, 1990). Tritium is therefore used simply to differentiate vintage waters, those recharged before 1952, and recent waters, those recharged after 1952. Groundwater containing less than 0.6 TU is thought to have originated prior to 1952. Groundwater with significantly higher tritium levels is post-1952 (Domenico and Schwartz, 1990). Assuming residence times greater than 45 years for groundwater sampled in this study, discharge areas should show low levels of tritium (less than 0.6 TU), and recharge areas should show substantially higher levels.

RESULTS AND DISCUSSION

St. George (1994) estimated recharge by numerically modeling groundwater flow over a variety of landforms in the Itasca moraine area. The results of the study show that the broad, level outwash plain south of the moraine is an area of very high recharge. These high values are in agreement with other studies of recharge on sandplains. Helgeson and

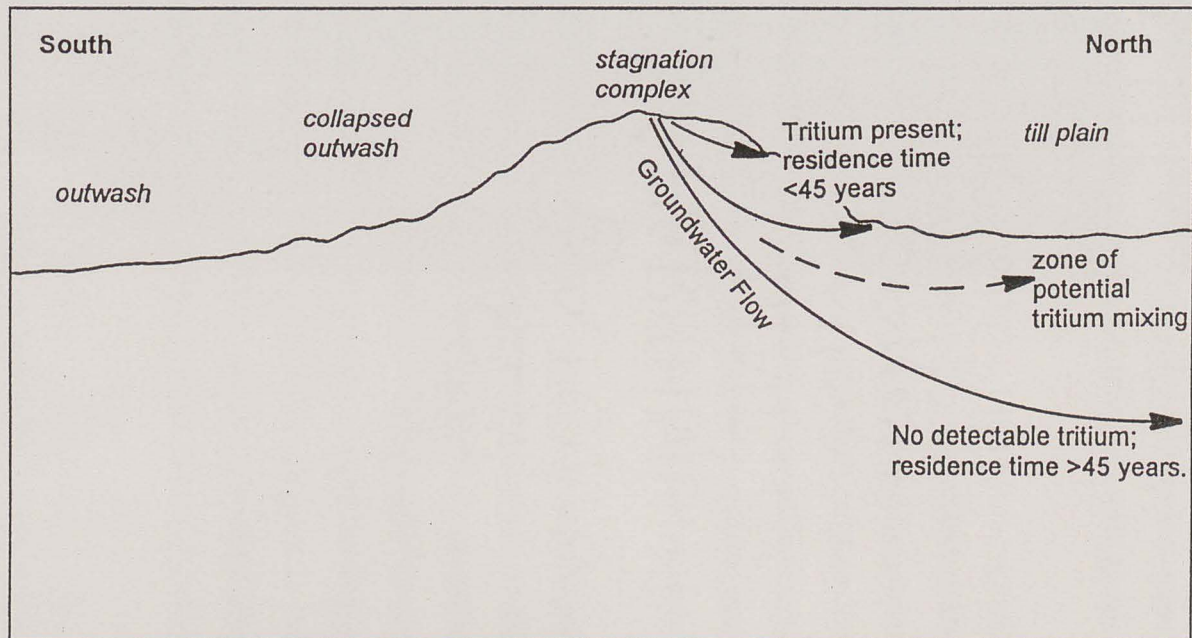


Figure 14. Mixing of waters with different tritium levels in hummocky topography.

Lindholm (1977) estimated recharge to be 30 cm/yr on the Anoka sandplain, and Wovcha (1989) calculated similar values on the Parkers Prairie sandplain in west-central Minnesota. The stagnation complex and collapsed outwash landforms the moraine comprises are areas of moderate recharge, and the till plain and lacustrine landforms to the north of the moraine constitute an area of very low recharge or discharge. The spatial distribution of landforms and corresponding recharge rates are shown on Figures 9 and 10, respectively.

This study examines the chemistry of waters collected from these landforms--specifically, the differences exhibited in the chemistry that may provide insight to relative rates of recharge to the intermediate and regional flow systems from these landforms. For the purposes of interpretation of recharge, four landform assemblages were chosen for evaluation: outwash, hummocky stagnation moraine, collapsed outwash (hummocky sandplain with abundant lakes), and till plain and lacustrine landform assemblages.

Certain data from the original 89 wells and 13 springs sampled are not considered in the following discussion. Six of the springs are located outside the study area. Several sites were located near boundaries between landform assemblages. One spring was sampled improperly, a common problem in the beginning of the study, particularly with dissolved oxygen samples, which are susceptible to contamination by atmospheric oxygen. Twelve sets of well data were thrown out for the same reason. Analyses from seven wells were eliminated because of rather large calculated electrical charge imbalances. The water from these wells was softened, and an accurate value for sodium was not obtained because of the high concentrations.

Field measurement of dissolved oxygen levels is sometimes complicated by contamination with atmospheric oxygen. Four D.O. samples are suspected to have been contaminated during collection. Three of these are springs from which the samples were pumped by

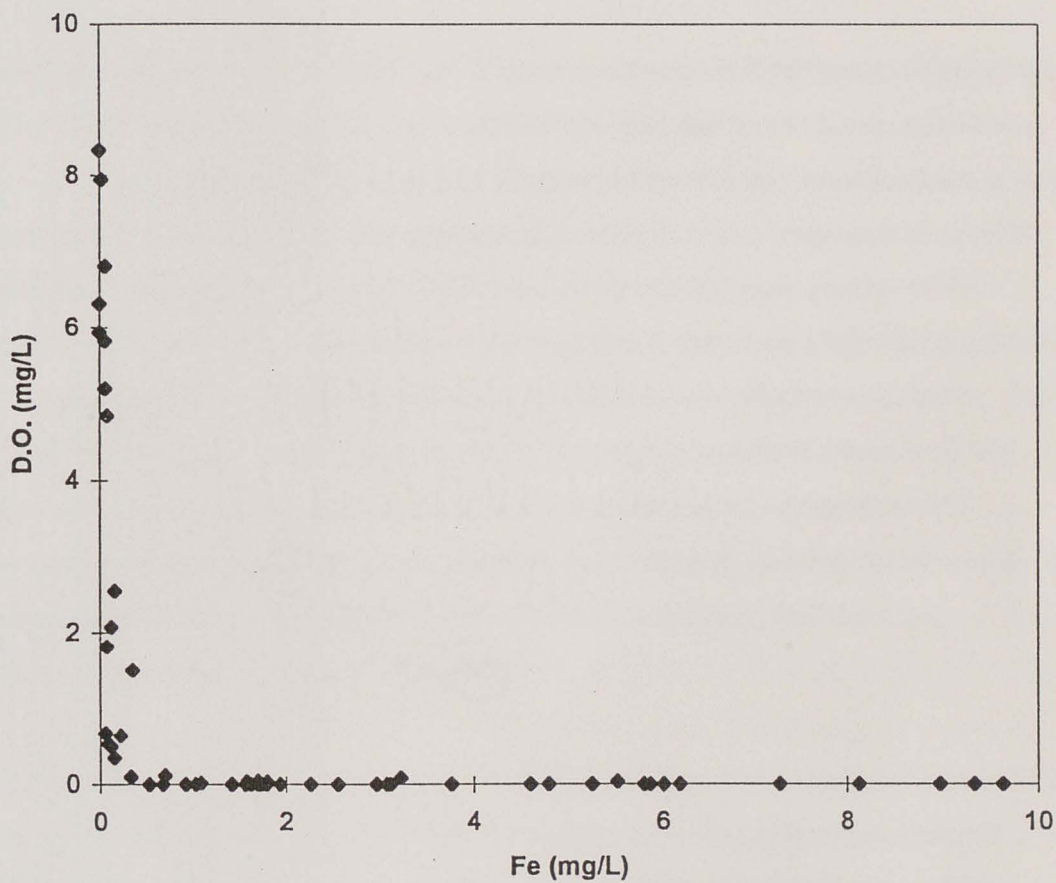
hand, making it difficult to maintain the level of flow necessary to keep air bubbles from entering the sample bottle. The fourth sample was possibly contaminated during collection from a hand-pumped well at which the same difficulty was encountered. An additional nine samples included in the final data set were collected early in the field season, before the collection procedure for D.O. samples was perfected. These samples were in contact with the atmosphere for an extended period prior to analysis.

Because of the relationship between dissolved iron and dissolved oxygen, iron values can be used as a means of determining D.O. concentrations. D.O. values from samples considered good analyses were plotted against iron (Figure 15). This graph shows that D.O. is negligible where iron concentration is greater than 1.0 ppm. D.O. values for the four spring and nine well samples mentioned above were assumed to be 0.00 mg/L, as they all have iron concentrations above 1.0 ppm. Samples with suspect D.O. values and iron concentrations less than 1.0 ppm were discarded.

In the final analysis, 64 sites were chosen for the ensuing discussion: 58 wells and six springs. Seventeen of these were classified as being in outwash, fourteen in the stagnation complex, fourteen in collapsed outwash, and nineteen in the till plain landform assemblages.

CHEMICAL EVOLUTION

Two distinct groundwater chemistries are evident in the samples. One chemistry is indicative of recent recharge and is termed "oxidized;" that is, it has high dissolved oxygen, low dissolved iron, high redox potential, and relatively low alkalinity. The other is a more evolved chemistry and is termed "reduced." Reduced chemistries are characterized by zero dissolved oxygen, high dissolved iron, low redox potential, and relatively high alkalinity. Tritium concentrations also distinguish oxidized waters from



reduced waters, which are, in some cases, inferred to be significantly older. There are, of course, some waters transitional between these two types, but a very distinct difference exists between oxidized and reduced chemistries.

REDOX CONDITIONS

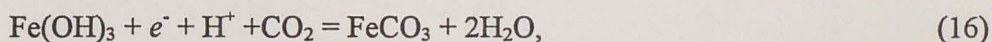
Dissolved oxygen, redox potential, and iron concentration are interdependent parameters. Where dissolved oxygen is high, redox potential is high, and iron concentration is low. The opposite is also true. High dissolved oxygen implies that the water has been in recent contact with the atmosphere. Precipitation, for example, is at or near saturation with dissolved oxygen. The high oxygen content of waters in the upper portion of the saturated zone corresponds to oxidizing conditions and, therefore, a high redox potential. Because conditions are oxidizing, the water is unable to hold free iron in solution. The water reaches equilibrium or supersaturation with respect to several iron-containing minerals at extremely low iron concentration. As the oxidation of organic matter consumes the dissolved oxygen, conditions become reducing, meaning the redox potential is low. Under these conditions ferrous iron is stable in solution, and there is a thermodynamic drive to dissolve iron minerals.

The redox potential, pH, and temperature of a solution determine the stability of mineral phases. An Eh-pH diagram constructed for a particular temperature represents the stability relations at equilibrium for a particular assemblage of minerals or species.

The prevalence of iron in the groundwater of this area and the large amount of carbonate in the drift necessitate the consideration of both iron and carbonate as factors affecting solution chemistry. The drift of the Itasca moraine area is rich in carbonate and iron-bearing minerals. The iron-bearing mineral phases include pyroxene, amphibole, and biotite as well as clasts of iron formation (Goldstein, 1985, 1989; Mooers, 1988; Gowan,

1993). In addition, weathering of iron-bearing minerals produces iron hydroxides, which commonly give soils and sediment within the oxidized zone their reddish-brown color (Buol et al., 1973). That portion of the total iron in sediment occurring as hydrous oxides and uncombined with layer silicate structures, and which is reductant soluble, is termed "free iron" (Buol et al., 1973, p. 69). These hydrous iron oxides commonly occur as discrete particles or as coatings on clays. Field investigations have described iron staining and iron concretions that have tentatively been identified as limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$) (H.D. Mooers, pers. comm.).

Given the relative abundance of free iron in a carbonate-buffered system, one can evaluate the stability fields for various iron species on an Eh-pH diagram for the Fe-O-H₂O-CO₂ system. The reactions controlling the stability between the phases of interest are: the reduction of ferric hydroxide to siderite,



and the reaction between siderite and aqueous ferrous iron, which occurs without a change in oxidation state,



The stability fields at 25 °C are shown on Figure 16. The actual temperatures of most of the sampled waters are closer to 10 °C. Garrels and Christ (1965) state, "A temperature change of a few degrees does not alter the [Eh-pH] diagrams more than the width of the lines used to indicate the phase boundaries." Obtaining accurate Eh values with which to create an Eh-pH diagram is problematic. Redox potential measured with a platinum electrode is not considered an accurate measure of the Eh of oxidizing solutions such as the oxidized waters under consideration here. According to Drever (1988), "In relatively oxidizing waters, Eh values measured with a platinum electrode can rarely be related to a specific redox pair and are rarely of much value in quantitative interpretations of natural water chemistry." However, it is evident that the Eh values for the oxidized waters are higher than those of reduced waters (Figure 16). Because precise values are not

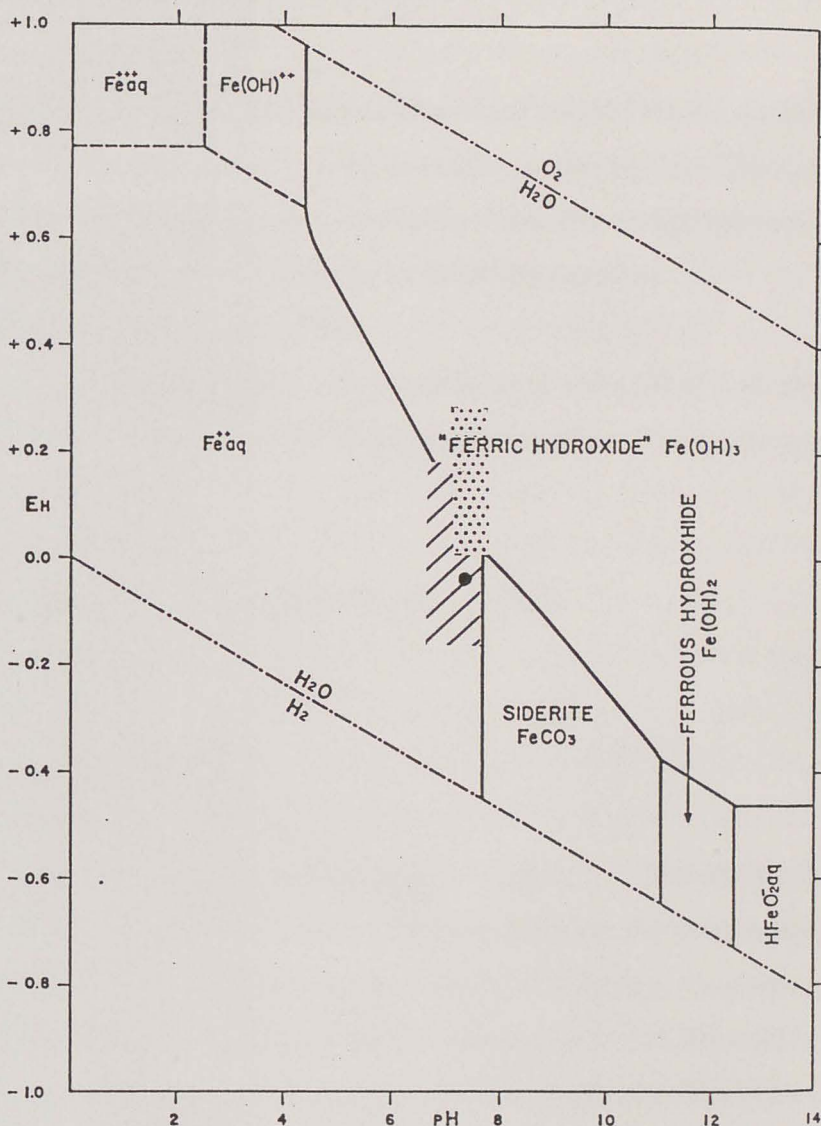


Figure 16. Eh-pH diagram for the Fe-O-H₂O-CO₂ system at 25 °C, 1 atm total pressure. Solid/solution boundaries represent $a_{\text{Fe}^{2+}} = 10^{-6}$. Rectangular areas encompass the range of data collected in this study. Oxidized chemistries plot within the stippled area, and reduced chemistries plot within the hatched area. The point represents an average pH for waters with a reduced chemistry and an Eh calculated from the ferric hydroxide-siderite redox couple (modified from Garrels and Christ, 1965).

measurable under these conditions, the entire range of values is plotted rather than specific points.

In order to verify the measured redox potentials of reduced waters, an Eh value is calculated for the ferric hydroxide-siderite redox couple (eq. 16). The equilibrium constant for this reaction, K_{eq} , is calculated by Gibbs free energy values obtained from Drever (1988). K_{eq} is related to pe by the following equation:

$$\log K_{eq} = pe + pH - \log PCO_2. \quad (18)$$

A PCO_2 of 10^{-2} , a typical value in the saturated zone, and a pH of 7.40, the average value for these reduced waters, are used in the calculation of pe. The equation relating pe to Eh is:

$$Eh = 0.059pe \quad (19)$$

(Drever, 1988). The results of the calculation follow:

$$\log K_{eq} = 8.77,$$

$$pe = -0.63,$$

$$\text{and } Eh = -0.037 \text{ V.}$$

Two fields are plotted on the stability diagram (Figure 16). One depicts the range of Eh and pH values measured in the oxidized waters, the other, the range measured in the reduced waters. Within the field of values for reduced waters, the point is plotted that corresponds to the average pH and the Eh calculated above (7.40, -0.037). It should be noted that the thermodynamic data upon which this calculation is based are not necessarily consistent with the data used to construct the stability diagram, and the actual position of this point on the diagram may vary slightly from that shown on Figure 16.

The oxidized waters plot within the stability field of ferric hydroxide, indicating this phase is stable with respect to ferrous iron or siderite under oxidizing conditions. This explains the low concentration of iron in solution in oxidized waters--it is in the form of ferric

hydroxide. The presence of ferric hydroxide is evident in the field. Dissolution of ferric hydroxide with decreasing redox potential is responsible for the increase in iron concentration in reduced waters. The reduced waters plot in the ferrous iron and siderite stability fields. Depending on the pH of the solution of these reduced waters, Fe^{2+} or FeCO_3 is stable with respect to ferric hydroxide. A plot of iron concentration vs. pH shows that above the bounding pH, 7.67, iron concentrations are less than those of reduced waters with pH below 7.67 (Figure 17). Aqueous iron is stable at the lower pH values, and siderite is stable at the higher pH values. Precipitation of siderite may account for the lower concentration of iron in solution above pH 7.67.

Stability diagrams illustrate which phases of the minerals and aqueous species are stable *under equilibrium conditions*. Kinetics dictates whether these reactions will actually proceed. For example, an increase in pH from 7.5 to 7.7 at an Eh of -0.1 V and constant PCO_2 should, according to the stability diagram, cause a thermodynamic drive to precipitate siderite. However, the kinetics must be favorable, or the iron will remain in solution. The decrease in iron concentration in reduced waters with pH greater than 7.67 discussed above suggests that precipitation of siderite is, in fact, taking place.

THE CARBONATE SYSTEM

The ubiquity of carbonate in the glacial drift of this area has a strong influence on the groundwater chemistry. All of the waters sampled are very hard, with values of total hardness ranging from approximately 190 to 400 ppm. They all have a Ca-Mg-HCO_3^- composition, and, at first glance, appear to be virtually indistinguishable from one another (Figure 18). However, there is evidence for evolution of the water in keeping with the conceptual model. Calcite dissolution produces bicarbonate as groundwater infiltrates carbonate-rich sediments, raising the alkalinity (eq. 9). This trend is accompanied by an increase in pH as calcite approaches saturation. The increase in pH observed from shallow

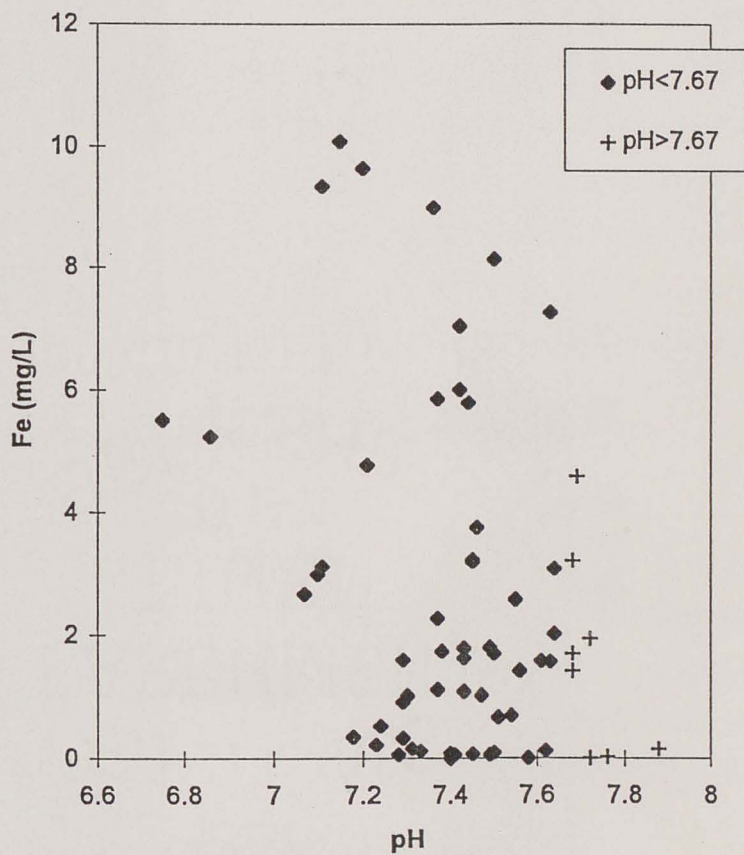


Figure 17. Iron concentration vs. pH.

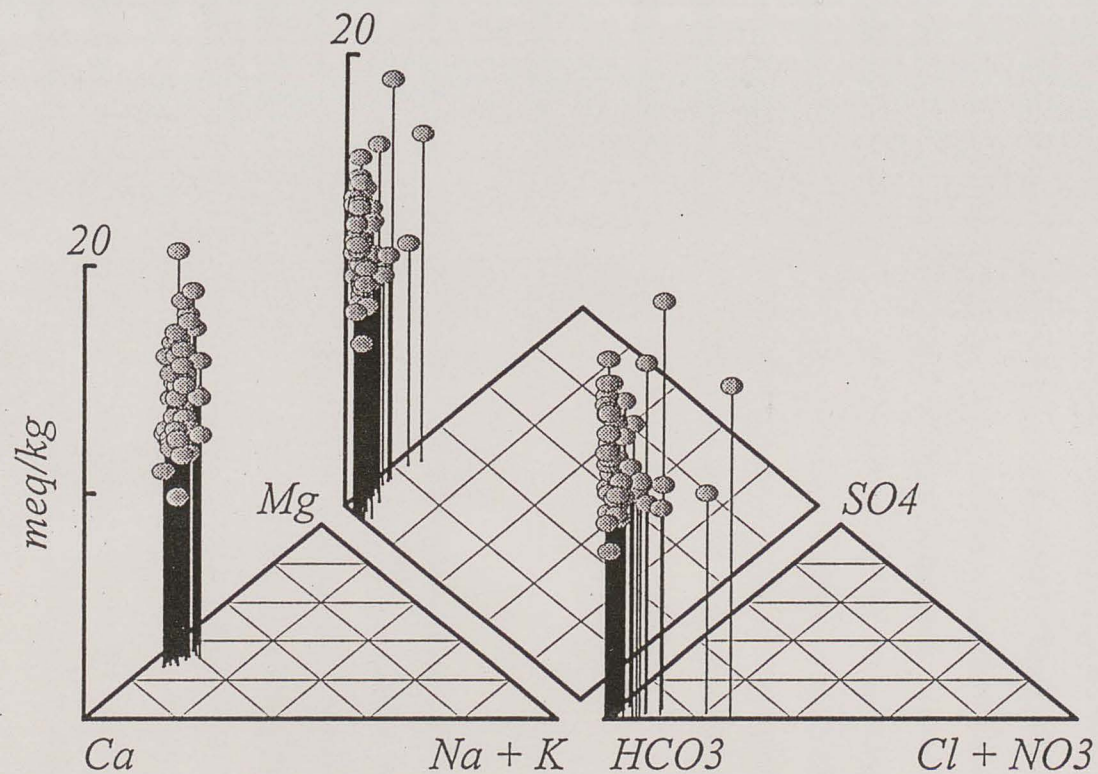


Figure 18. 3-D Piper diagram of cation and anion analyses. Vertical scale shows concentration of dissolved solids.

(usually oxidized) to deep (usually reduced) waters is shown on Figure 19. The increase in alkalinity as groundwater evolves is also apparent. Alkalinity trends are discussed in the context of individual landforms below.

ENVIRONMENTAL ISOTOPES

Environmental isotopes can be helpful in distinguishing between oxidized and reduced chemistries. There is a linear relationship between $\delta^{18}\text{O}$ and δD in precipitation of specific regions. Water samples that plot along this line are considered to be meteoric. All of the samples collected for the analysis of ^{18}O and D plot very close to the meteoric water line (Figure 20). Tritium serves to distinguish waters that were recharged prior to 1952 from waters recharged since 1952. A wide range of tritium values occurs in the seven samples analyzed, indicating that both vintage and recent waters exist in the unconfined drift aquifer. The tritium results will be considered individually in the landform-based geochemical interpretation below.

AQUEOUS SPECIATION

Three sites were chosen to illustrate the chemical evolution of groundwater by means of aqueous speciation. The first is LI 0894 07R, a 51-foot well in the northern part of the moraine. It has an oxidized chemistry and is intended to represent a recently recharged water. The second is LI 0894 119, a 90-foot well, also located in the northern part of the moraine. It was chosen for two reasons. It has a reduced chemistry, and it is located near 07R. The water from which it has evolved is probably similar to that of 07R. The third site is a typical discharge water, Iron Spring, LI 0794 52. It is located near 119 and 07R and is hydraulically downgradient from them. The location of the three sites and a map of the water table are shown on Figure 21.

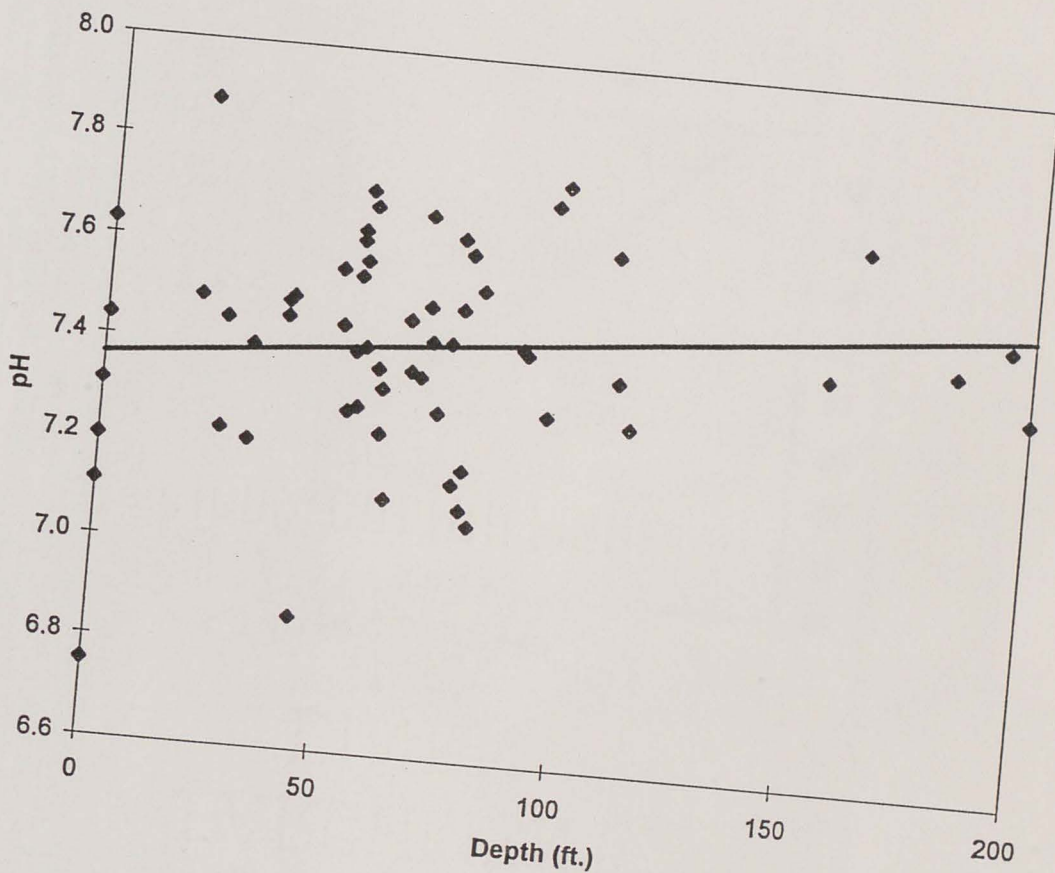


Figure 19. pH vs. depth of groundwater sampled. Regression line shows increasing pH with depth.

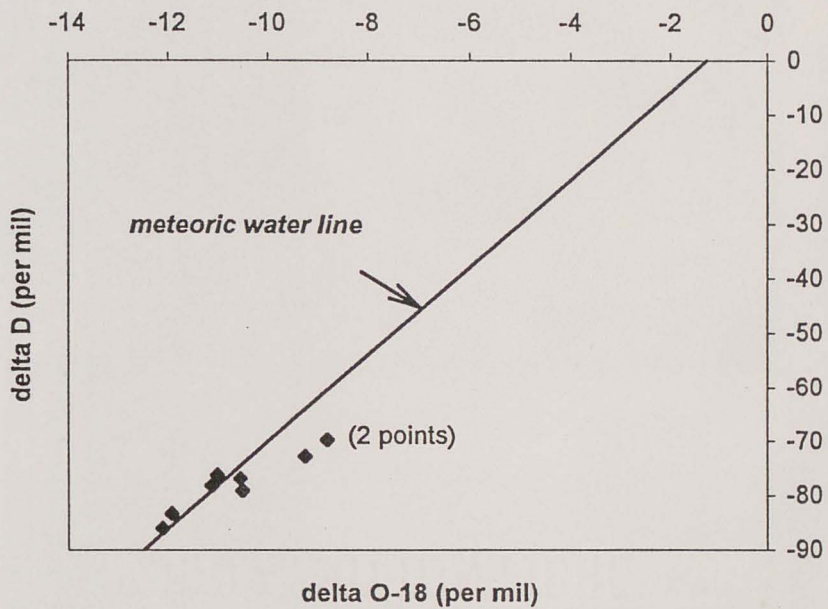
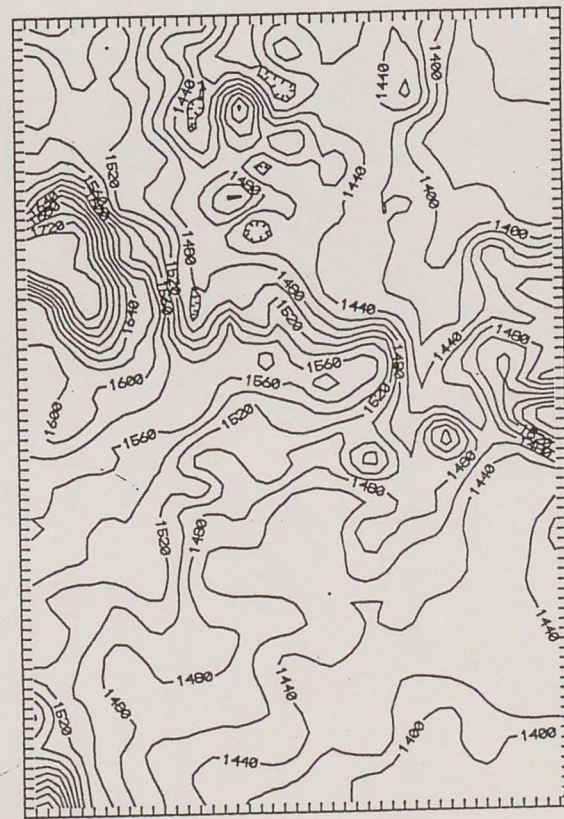
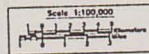
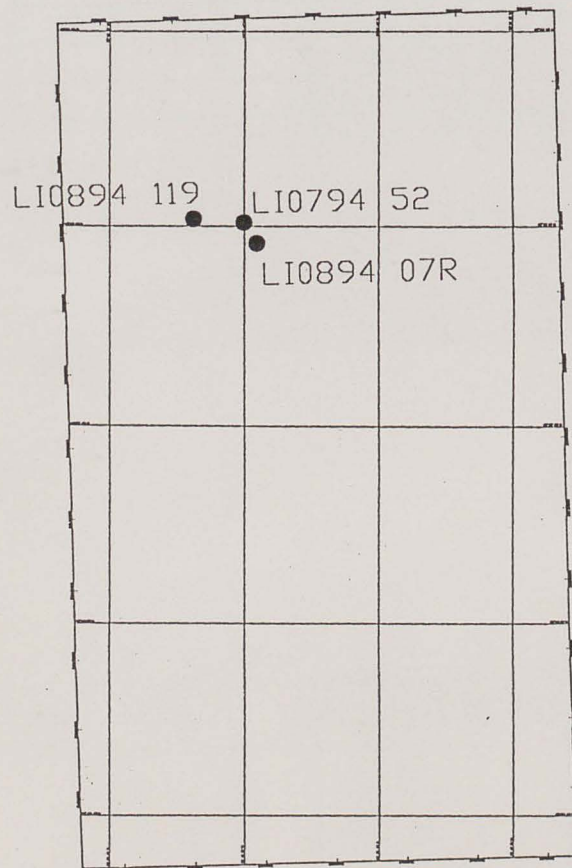


Figure 20. $\delta O-18$ and δD variations in groundwater sampled.



contour interval = 20 feet

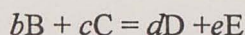
5 Km

Figure 21. Location of samples speciated by EQ3 (modified from St. George, 1994) and contoured water table elevations (from St. George, 1994).

Saturation indices calculated by EQ3 quantify the degree of saturation of the solution with respect to various minerals. Freeze and Cherry (1979) define the saturation index as

$$S_i = Q / K_{eq},$$

where Q is the reaction quotient defined for the reaction



in a state of disequilibrium, as

$$Q = \frac{[B]^b [C]^c}{[D]^d [E]^e}.$$

EQ3 reports saturation indices as logarithmic values, and, as such, $S_i = 0$ represents saturation, $S_i > 0$, supersaturation, and $S_i < 0$, undersaturation. Supersaturation with respect to a particular mineral indicates a thermodynamic drive to precipitate that mineral. Conversely, undersaturation indicates a thermodynamic drive to dissolve the mineral. Saturation indices for minerals expected to control most chemical reactions are shown on Table 1. Analytical concentrations of alkalinity and cations added to or taken from solution as a result of dissolution or precipitation of these minerals are shown on Table 2.

	07R: Oxidized	119: Reduced	52: Discharge
Calcite	0.04	0.23	0.18
Dolomite	0.88	1.3	1.2
Silica (am)	-0.68	-0.59	-0.5
Fe(OH) ₃	-1.4	-4.3	-3.1
Siderite	-1.3	0.71	0.64
Hematite	8.9	3.0	5.4
Magnetite	6.3	2.2	4.5

Table 1. Saturation indices (in logarithmic form) for selected minerals as calculated by EQ3.

	07R: Oxidized	119: Reduced	52: Discharge
Alkalinity	238	335	333
Ca	65.22	82.34	80.38
Mg	20.05	26.53	26.72
Si	6.85	8.78	9.48
Fe	0.07	6.01	5.80

Table 2. Analytical concentrations of alkalinity (ppm as CaCO_3) and selected cations (mg/L).

Calcite increases from 0.04, essentially saturation, to slight oversaturation as the water evolves with increasing residence time along a flowpath. This implies that equilibrium with respect to calcite is reached very quickly upon infiltration. Dissolution continues to occur with increasing residence time, as indicated by increasing calcium concentration. Dolomite in this system experiences the same fate. According to the saturation indices, dolomite becomes increasingly oversaturated as the water evolves. The concentration of magnesium also increases from oxidized to reduced and discharge waters. The saturation index for amorphous silica increases from undersaturation in the oxidized water to a value closer to saturation in the reduced and discharge water, indicating possible chert dissolution. This is consistent with increasing silica concentrations along the flowline. However, the chemical alteration of feldspars to clay minerals may cause a similar increase in silica concentration (Drever, 1988).

Saturation indices of ferric hydroxide and siderite agree with the conclusions drawn from the Eh-pH diagrams previously discussed. In the oxidized water ferric hydroxide is slightly undersaturated. Waters with reduced chemistries are greatly undersaturated with respect to ferric hydroxide, indicating a thermodynamic drive to dissolve. Ferric hydroxide is not stable under these conditions and is reduced to the soluble ferrous state in the form of aqueous ferrous iron or siderite. Siderite is undersaturated in the oxidized water and becomes supersaturated at depth, indicating that precipitation should occur if kinetically uninhibited. The large increase in iron concentration with residence time

verifies the tendency toward iron dissolution along a flowpath. Saturation indices for both hematite and magnetite show that they evolve from states of extreme to moderate supersaturation, indicating a drive to precipitate. Kinetics may obviate this process, however, particularly on time scales this short and with temperatures this low.

LANDFORM-BASED INTERPRETATION OF GROUNDWATER CHEMISTRY

OUTWASH LANDFORM ASSEMBLAGES

What are considered outwash sediments in this study include St. George's outwash plain and outwash fan landforms in the southern portion of the study area (Figure 9). Outwash sediments are moderately well- to well-sorted sands with some gravels. The topography is mostly level with occasional closed depressions, but in some places it is gently sloping with numerous closed depressions. Mean hydraulic conductivity is in the order of 10^{-2} cm/s, the highest of the landforms in this area (St. George, 1994) (mean hydraulic conductivity is shown on Figure 22). These properties allow precipitation to infiltrate rapidly, resulting in a high value of recharge over these sediments (Stark, et al., 1994; St. George, 1994). St. George estimated recharge rates of 15-21 cm/yr.

A thick, fairly uniform oxidizing zone occurs throughout these high-recharge landforms. Wells producing water with an oxidized chemistry are screened in the oxidizing zone, while wells producing water with a reduced chemistry are screened in the reducing zone. In a few places, two wells of similar depth were sampled in close proximity to one another, one screened in the oxidizing zone, the other in the reducing zone. This allowed the redox boundary to be bracketed between the two depths. A cross-section including three sets of these conjoint pairs is shown on Figure 23. The redox boundary is located at a depth of about 55 feet. One particularly notable pair of wells is LI 0794 53 and 54, Guinn #1 and Guinn #2. These two wells are roughly 100 meters from each other and are

LEGEND TO ACCOMPANY FIGURE 22

Landform Number	Landform	Hydraulic Conductivity (cm/s)
1	Till Plain (Wadena Lobe)	6.65 E-05
2	Till Plain (Koochiching Lobe)	3.21 E-05
3	Stagnation Complex	
3a	Main Complex	4.25 E-04
3b	Anchor Hill I	4.25 E-04
3c	Anchor Hill II	4.25 E-04
3d	Smoky Hills	4.25 E-04
4	Lacustrine Sediment	4.74 E-04
5	Outwash Channel	1.03 E-02
6	Collapsed Outwash	7.20 E-03
7	Outwash Fan	2.09 E-02
8	Outwash Plain	5.37 E-02

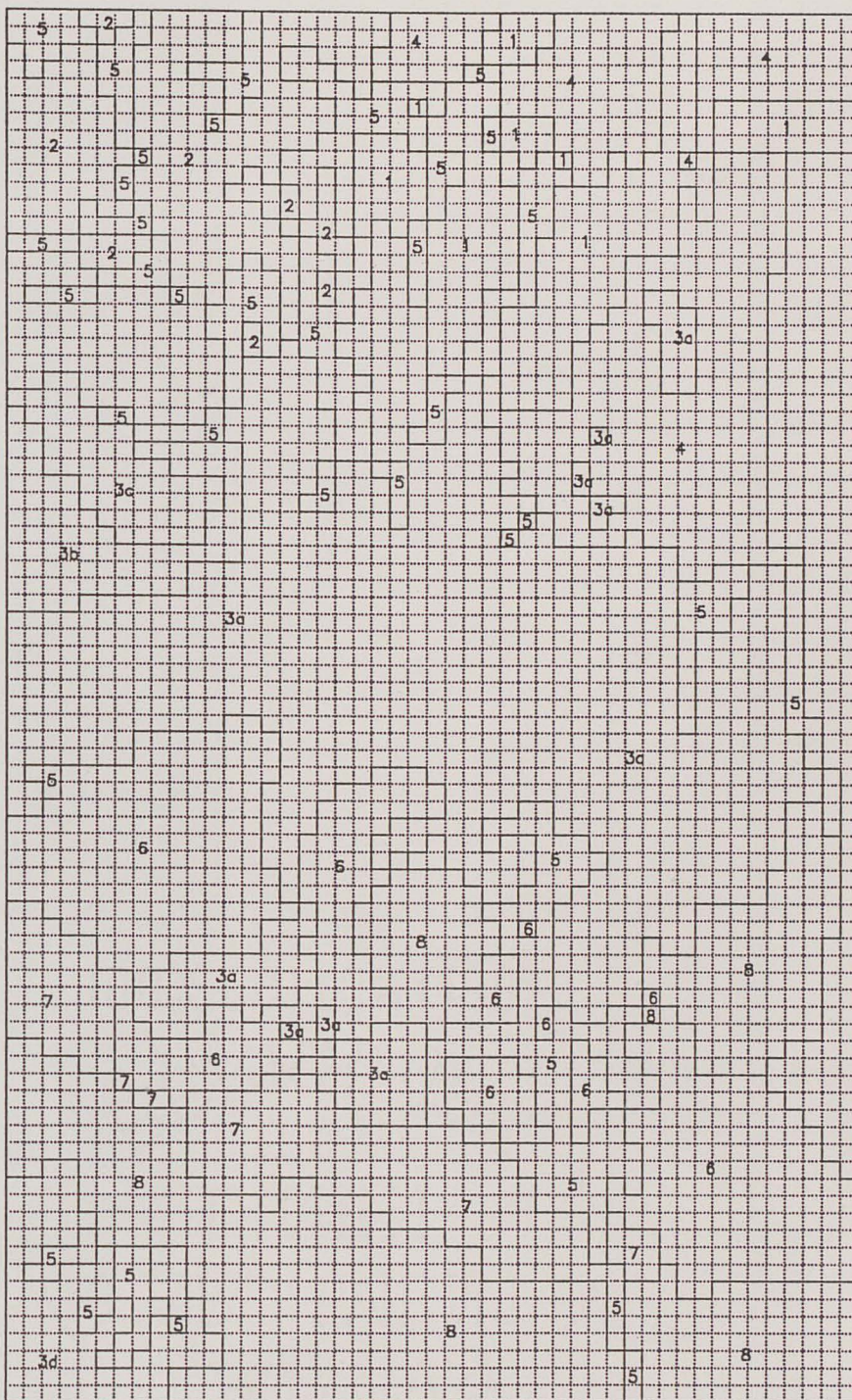


Figure 22. Mean hydraulic conductivity of landform assemblages (from St. George, 1994).

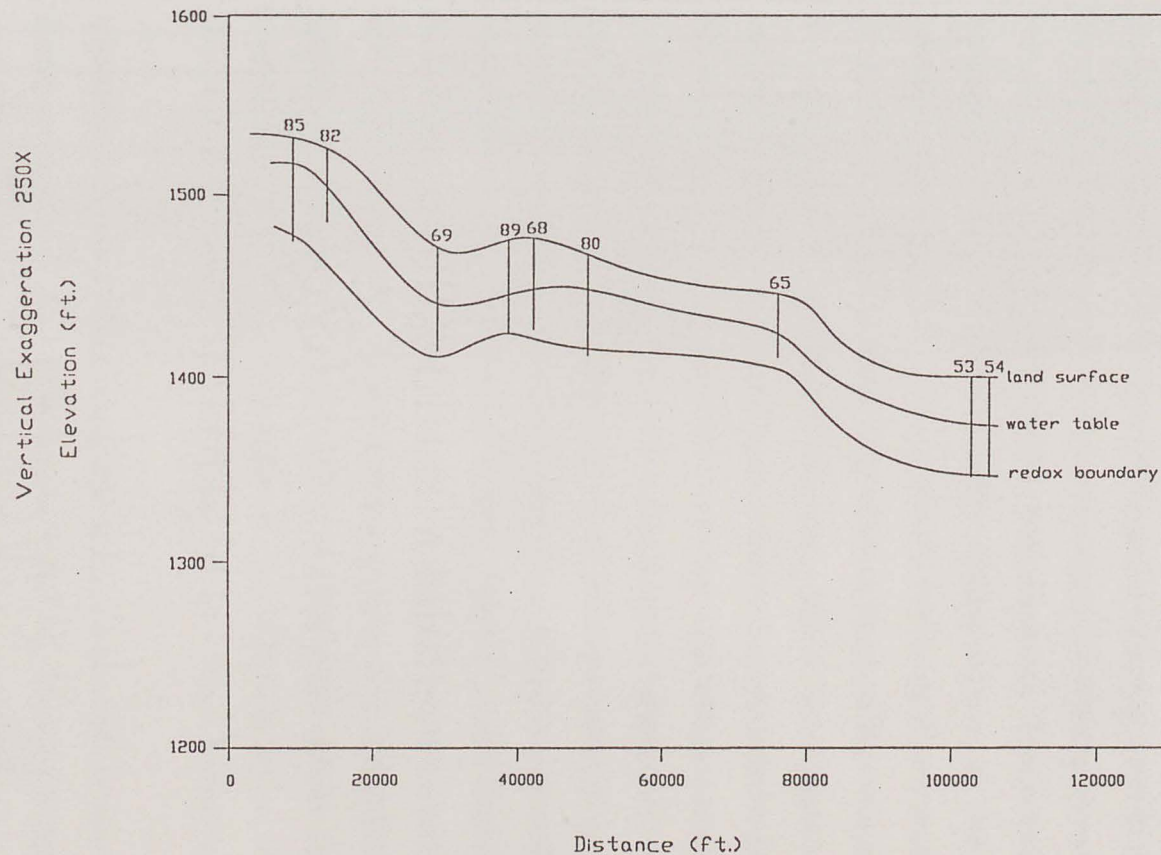


Figure 23. Cross-section illustrating the oxidizing zone in outwash landform assemblages. Well numbers correspond to the last digits of the site number.

approximately the same depth. One is in the oxidizing zone, and one is in the reducing zone. The redox boundary at this location can be estimated with some certainty at 55 feet, the approximate depth of the wells.

The plot of dissolved oxygen vs. depth also illustrates the thickness of the oxidizing zone (Figure 24). Below depths of about fifty feet dissolved oxygen is absent. The wells producing water containing dissolved oxygen are drawing water from the oxidizing zone. Those producing water with no dissolved oxygen are drawing water from the underlying reducing zone, in which the oxygen has been consumed. Two wells shallower than fifty feet appear to have anomalous low values of dissolved oxygen. One is a twenty-foot well containing 0.35 mg/L D.O., which is actually a fairly significant amount. This well is located in a depression surrounded by hills near the boundary between collapsed outwash and outwash fan. It is possible that the nearby hills of the collapsed outwash are receiving recharge by infiltration of precipitation, which is then being discharged at the base of the hill after a short residence time. The water may have infiltrated to a depth below the redox boundary and flowed upward to the twenty foot depth from which it was drawn. This concept will be explained in more detail in the discussion of the hummocky supraglacial drift complex landform assemblage. A 39-foot well in the outwash sediments also shows an absence of dissolved oxygen. This may be due simply to a local thinning of the oxidizing zone. This particular well was sampled for tritium and has a concentration of 46 TU. The water was therefore recharged after 1952, and probably does not owe its reduced chemistry to a long flowpath within a larger flow system. One of the deep wells shows a D.O. of 1.5 mg/L. This again may be attributable to local variation in the thickness of the oxidizing zone, or it may be due to contamination during sampling.

Alkalinity values support the change in chemistry with depth in these sediments. As shown on the plot of alkalinity vs. depth (Figure 25), alkalinity is highest in the deepest well. This follows the conceptual model in that dissolution of carbonates, which are

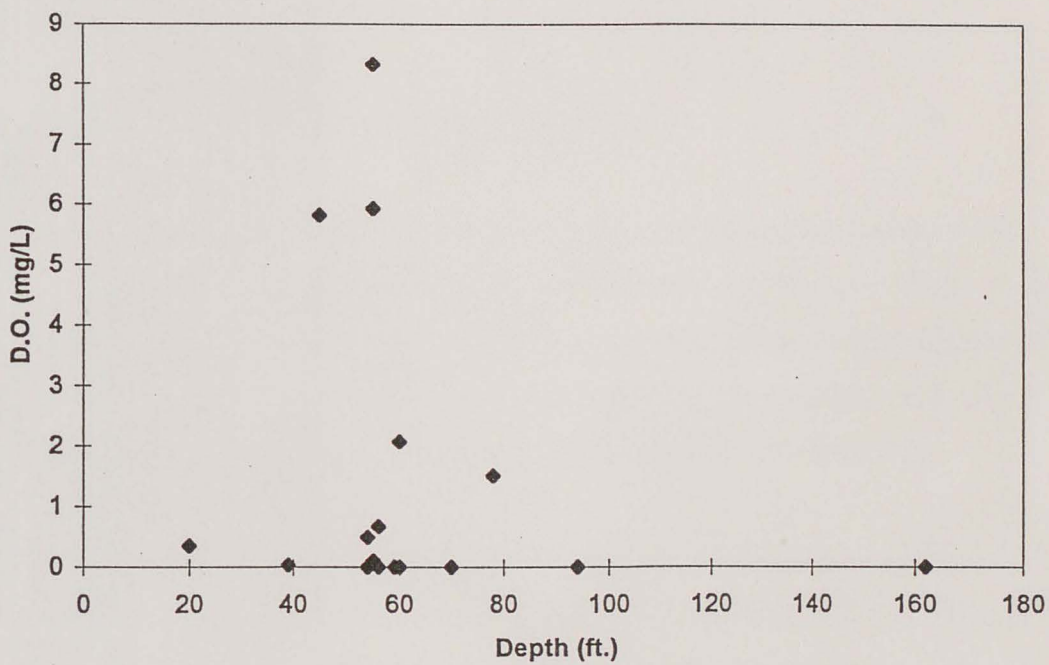


Figure 24. Dissolved oxygen vs. depth in outwash landform assemblages.

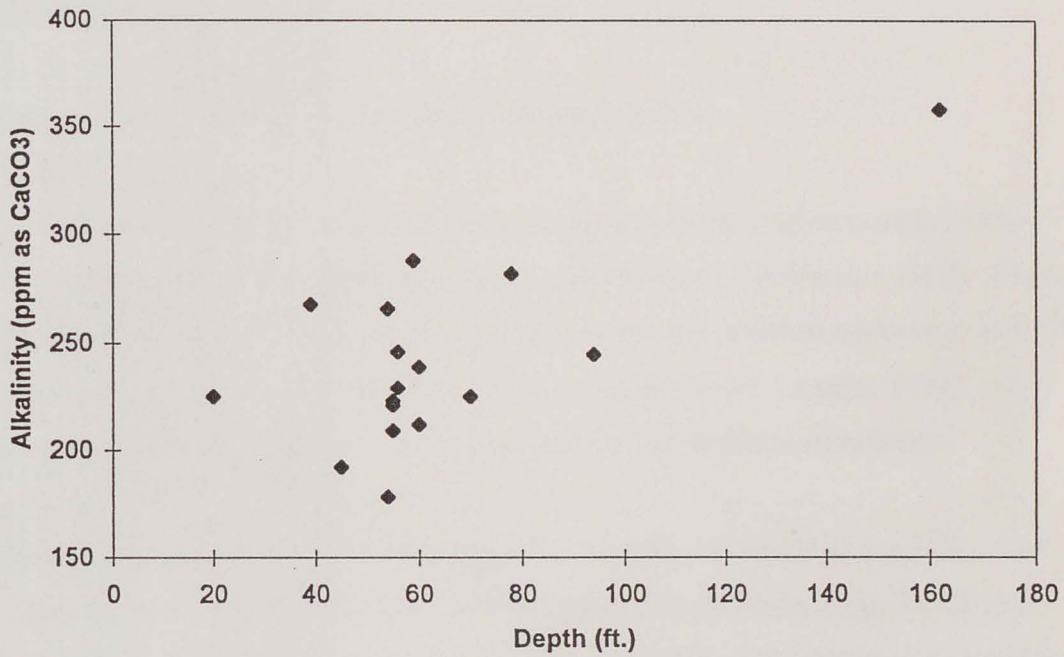


Figure 25. Alkalinity vs. depth in outwash landform assemblages.

present in large amounts in the drift, produces bicarbonate. As the water infiltrates the drift and more and more carbonate is dissolved, alkalinity increases. At the pH of these waters alkalinity is almost entirely a result of bicarbonate. Calcium mimics this increase in concentration (Figure 26).

Tritium analysis of sample LI 0794 81, a well 162 feet deep, shows a tritium concentration of 0 TU. The absence of tritium indicates that the water drawn from this well was recharged prior to 1952 and is therefore vintage.

HUMMOCKY STAGNATION COMPLEX LANDFORM ASSEMBLAGE

The sediment type and grain sizes of drift in the hummocky stagnation complex of the Itasca moraine are more variable than the outwash sediments (St. George, 1994). They range from well-sorted to silty sands to sandy loam tills and unsorted sand and gravel with a mean hydraulic conductivity of 4.25×10^{-4} cm/s (Figure 22) (St. George, 1994). St. George estimated a moderate 1.2 cm/yr recharge for this landform assemblage.

The topography in this area is hummocky with many hills and closed depressions. The hummocky nature of the topography and the high relief result in the formation of local flow systems. Tóth (1963) characterized local, intermediate, and regional flow systems on the basis of relief and topography. Tóth defines a local system as one in which recharge occurs at a topographic high and discharge occurs at an adjacent topographic low. Intermediate flow systems have at least one topographic low separating the recharge and discharge areas. In regional flow systems recharge occurs at a groundwater divide, and discharge occurs at the low of the basin (Figure 27). Tóth also observes, "increasing topographic relief will tend to increase the depths and the intensities of the local flow systems."

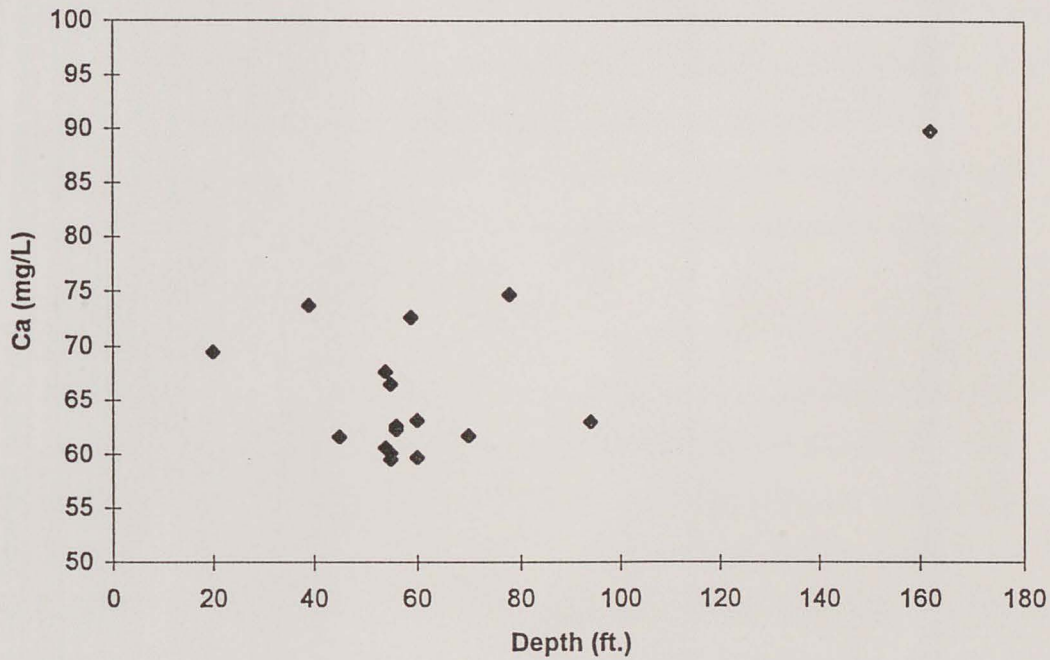


Figure 26. Calcium concentration vs. depth in outwash landform assemblages.

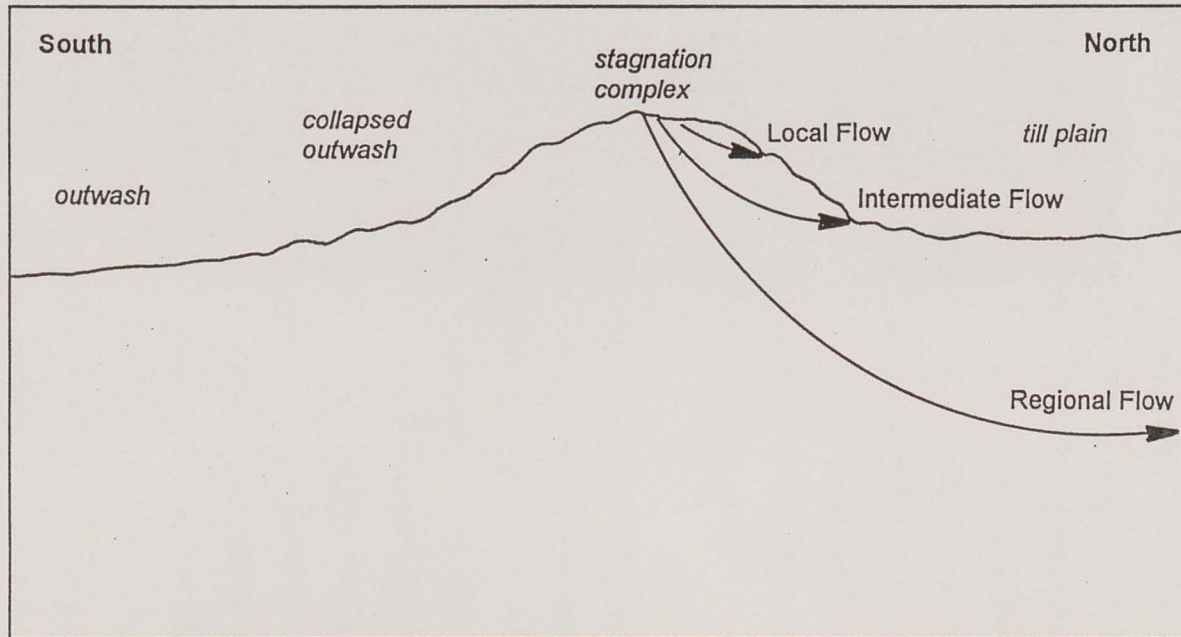


Figure 27. Regional, intermediate, and local flow systems in hummocky topography (based on Tóth, 1963).

Several studies following Tóth's expand on this concept, applying the theory to specific flow systems. Meyboom (1966 and 1967) studied the seasonal variations of discharge in temporary sloughs (1966) and permanent lakes (1967) in a hummocky moraine of Saskatchewan. The basis of this study is that within hummocky topography, all lakes and sloughs are manifestations of groundwater discharge, be it local, intermediate, or regional. Maclay and Winter (1967) relate the geochemical evolution of groundwater to the magnitude of the flow system in western Minnesota. Zebarth and DeJong (1989) studied flow systems surrounding two sloughs in hummocky topography of Saskatchewan, and confirmed the role of upland areas in hummocky topography as regions of local groundwater recharge. St. George (1994) suggested that the moderate recharge values calculated for the hummocky stagnation complex in this study area were a result of evaporative pumping from lakes and swamps.

The plot of dissolved oxygen with depth follows the general trend of reducing conditions with depth (Figure 28). Two wells less than fifty feet deep have high D.O. values typical of oxidized water, and several deeper wells have low D.O. values indicative of reduced water. There are two springs shown in the data set, Basswood and Elk Lake Springs, containing no dissolved oxygen. These are waters that have recharged in the topographic highs of the moraine, infiltrated the drift, and are now being discharged from depth at topographic lows. They exemplify a reduced chemistry--no dissolved oxygen and a high concentration of iron. However, a third spring, Nicollet Spring, has a moderate amount of dissolved oxygen and a relatively low concentration of iron. These conditions suggest that Nicollet Spring is discharging water from a smaller flow system than the other two, i.e., a local flow system with a short residence time. This is verified by the concentration of 27.5 TU tritium in the water, which indicates recent recharge.

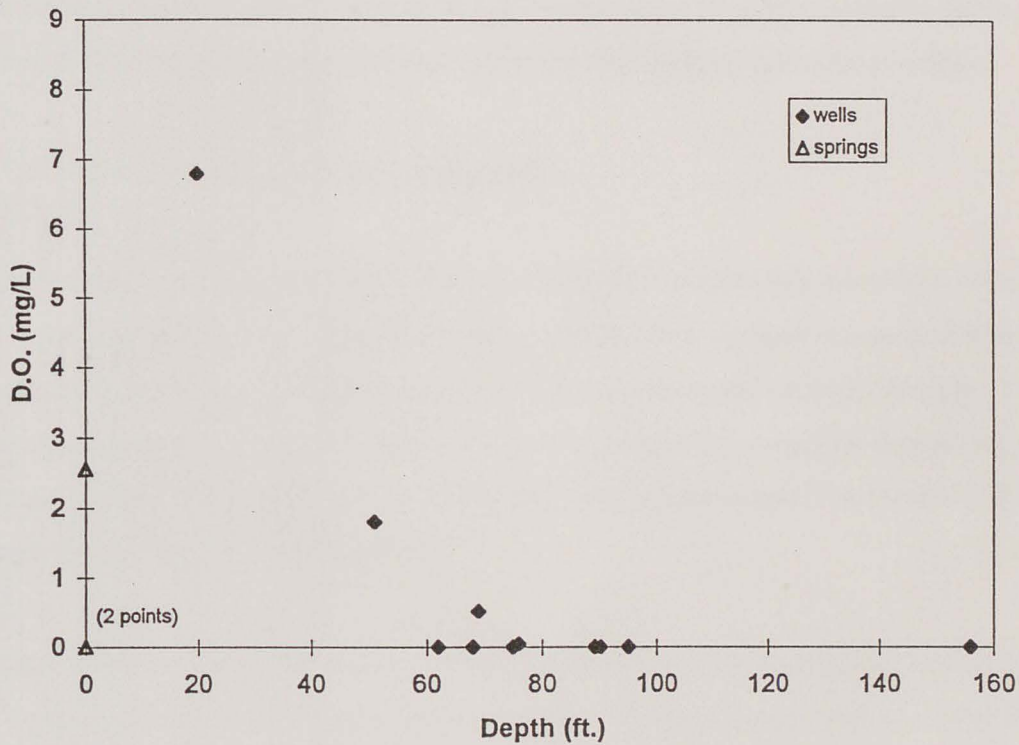


Figure 28. Dissolved oxygen vs. depth in hummocky stagnation complex landform assemblage.

Alkalinity values corroborate this observation (Figure 29). Nicollet Spring has a much lower alkalinity (210 ppm as CaCO_3) than Basswood and Elk Lake springs (294 and 335 ppm as CaCO_3 , respectively). Alkalinity values of water from wells within the hummocky stagnation complex appear to increase with depth.

The chemical evolution of groundwater in the hummocky stagnation complex follows the expected changes in groundwater chemistry between oxidized and reduced waters.

COLLAPSED OUTWASH LANDFORM ASSEMBLAGE

The recharge rate calculated by St. George (1994) for the collapsed outwash is 7.6 cm/yr, intermediate between the stagnation complex and the outwash landform assemblages. The sediments, however, are similar to outwash--mostly well-sorted sand (St. George, 1994). The topographic expression is similar to that of the stagnation complex--hummocky with closed basins. The mean hydraulic conductivity of these sediments is in the order of 10^{-3} cm/s (Figure 22) (St. George, 1994).

Figure 30 shows the relation of dissolved oxygen vs. depth for a spring and several wells. The spring is interpreted as a discharge point of a local flow system, and has a chemistry typical of a reduced water. Four shallow wells also have reduced chemistries. These, too, are interpreted to be located in areas of local discharge; one is located in a low marshy area, and three are located near lakes. Sample LI 0794 48R, a 26-foot well, has a tritium value of 9.0 TU, indicating that, although the reduced chemistry denotes discharge, the residence time has been relatively short. A shallow well with an oxidized chemistry (Figure 30) is simply drawing water from the oxidizing zone. Similarly, the deep wells with reduced chemistries are drawing water from the reducing zone. The deep well with

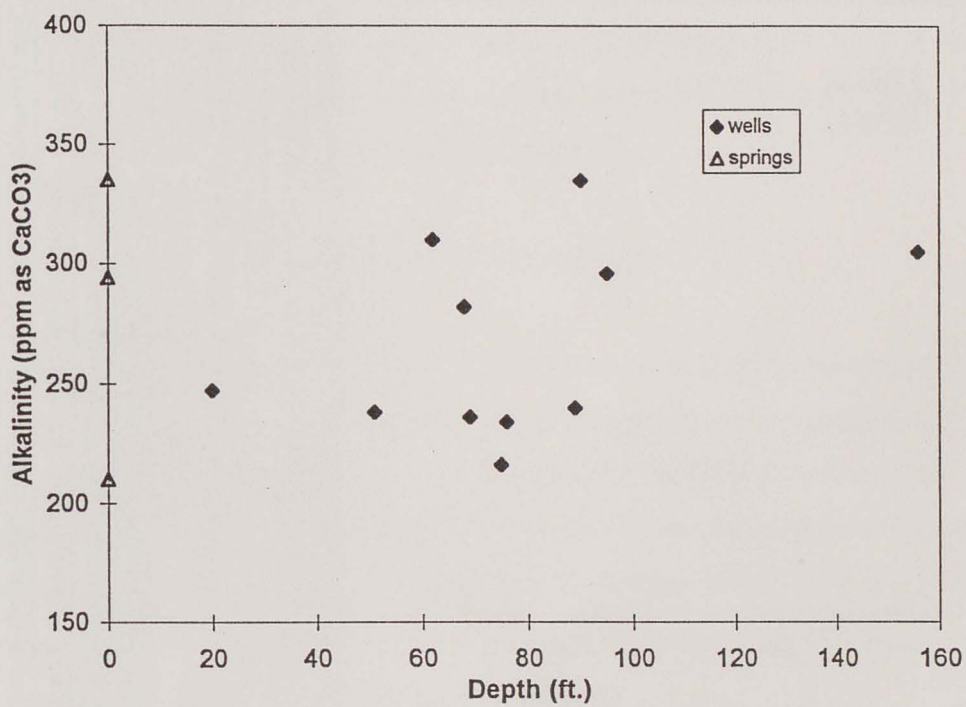


Figure 29. Alkalinity vs. depth in hummocky stagnation complex landform assemblage.

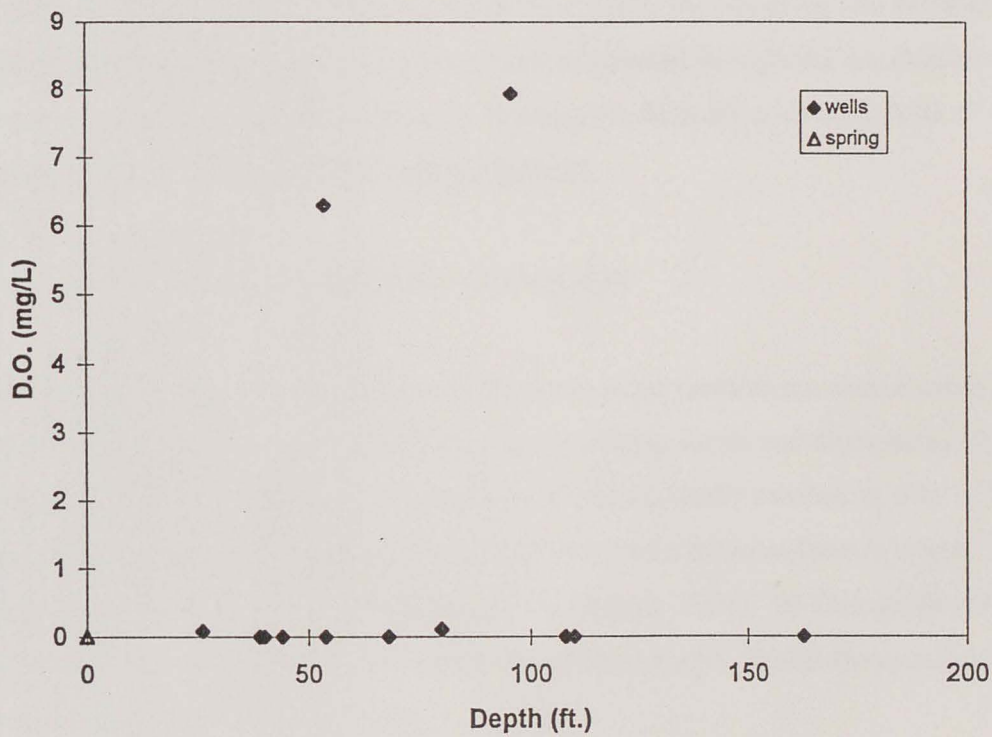


Figure 30. Dissolved oxygen vs. depth in collapsed outwash landform assemblage.

oxidized chemistry is drawing water from the oxidizing zone, possibly because the depth to water is greater in this area, as the well is located on a topographic high.

Alkalinity decreases with depth in these sediments (Figure 31). This is the opposite of what is normally expected, but the residence times of these waters also decrease with depth. The shallow wells are drawing water from the discharge end of a flowpath, whereas the deeper wells are drawing water from nearer the beginning of a flowpath--water that has infiltrated from its recharge area downward through the unsaturated and saturated zones, but has not begun to move along the flowpath toward its point of discharge. This concept is illustrated on Figure 32.

TILL PLAIN AND LACUSTRINE LANDFORM ASSEMBLAGES

The till plain and lacustrine landforms to the north of the moraine are characterized by undulating topography with low relief and gently sloping swells and depressions (St. George, 1994). In general, there is a uniform till cover, locally overlain by silty or loamy sand lacustrine sediment. Hydraulic conductivity of most of the sediments is low, approximately 10^{-5} to 10^{-4} cm/s (Figure 22) (St. George, 1994). St. George identifies these landforms as areas of no recharge or negative recharge. Within the area flowing wells, springs, and marshes abound.

The chemistry of waters in these landforms is reduced with few exceptions. Dissolved oxygen values (Figure 33) are zero for samples collected from springs and shallow and deep wells alike. The abundance of flowing wells and springs indicates that this area is characterized by upward hydraulic gradients and groundwater discharge. Upward movement of reduced waters results in the absence of an oxidizing zone; conditions are reducing right to the land surface, since there is no oxygenated water recharging the system. This concept is illustrated schematically on Figure 34. These waters have

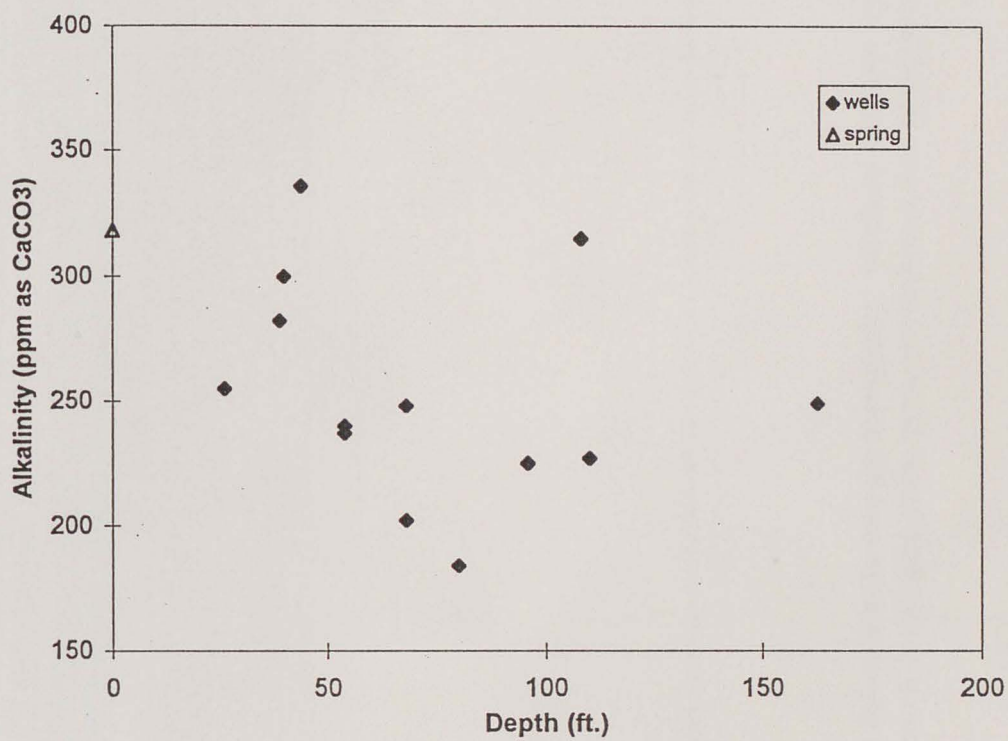


Figure 31. Alkalinity vs. depth in collapsed outwash landform assemblage.

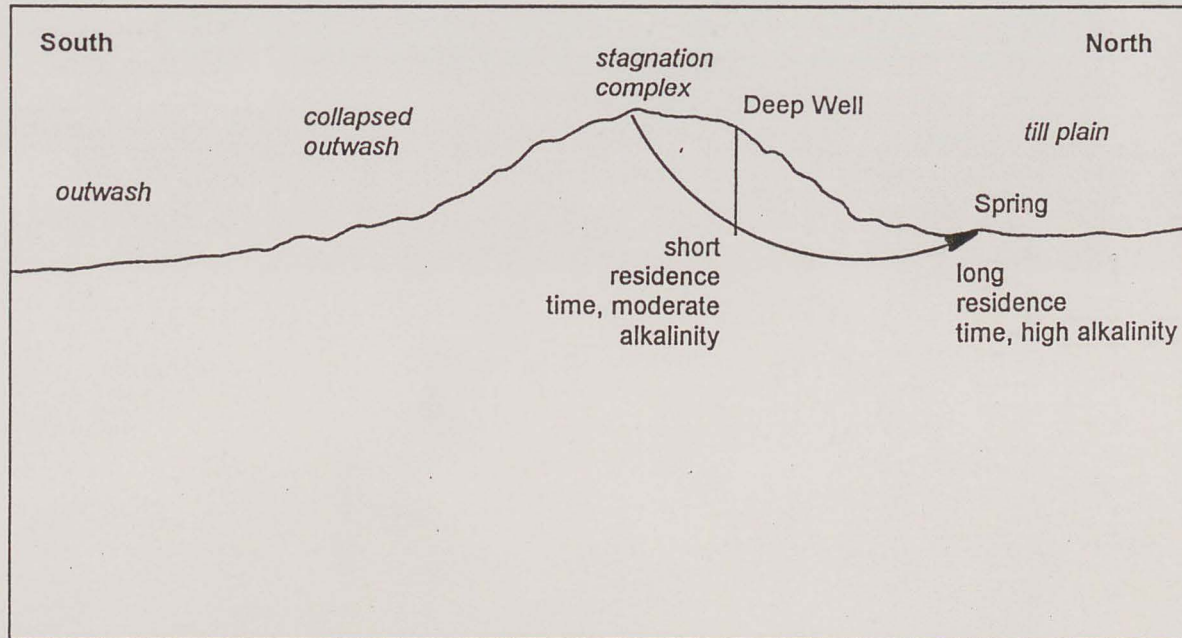


Figure 32. Alkalinity increase along a flowpath in hummocky topography. Alkalinity increases with residence time, not necessarily depth. In this case groundwater discharging at the spring has had more time to interact chemically with the aquifer materials.

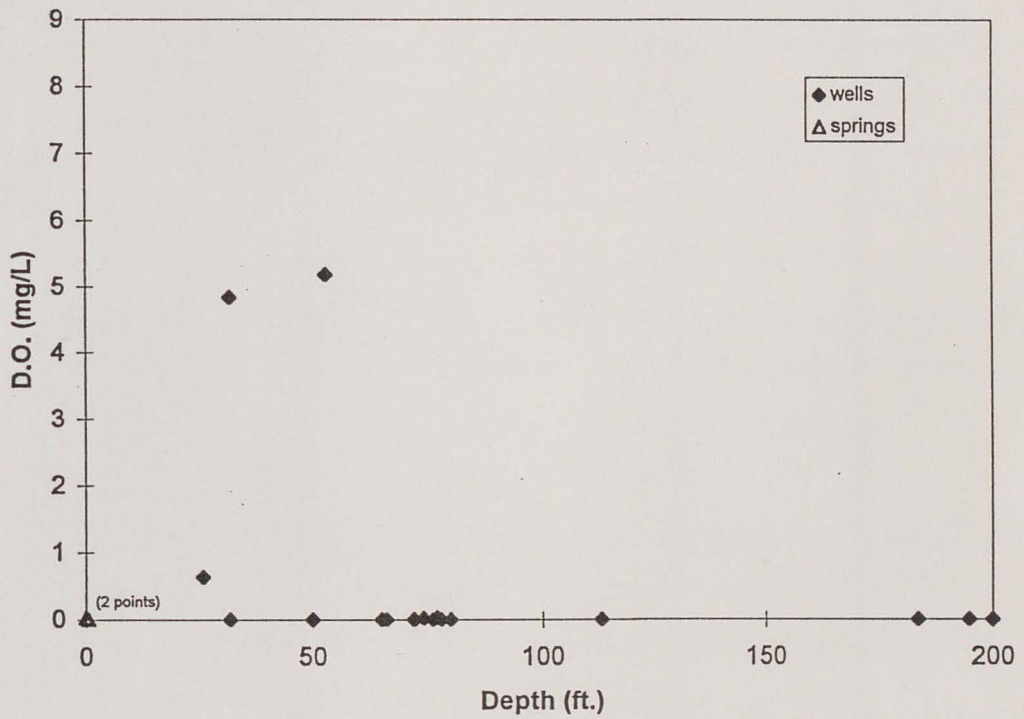


Figure 33. Dissolved oxygen vs. depth in till plain and lacustrine landform assemblages.

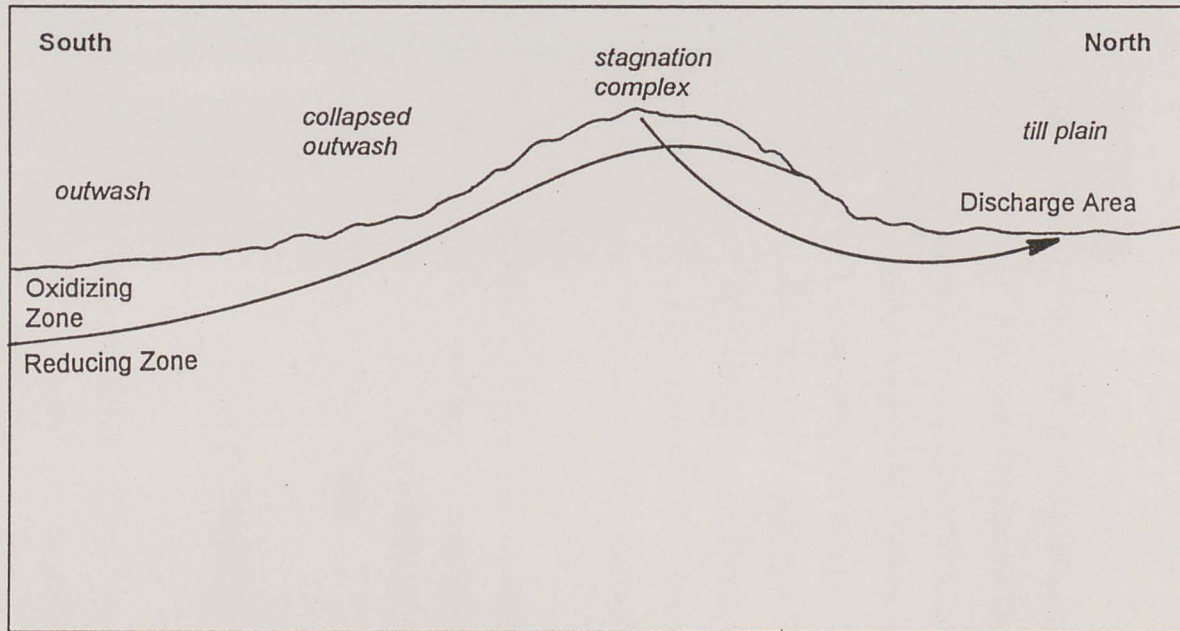


Figure 34. Cross-section illustrating the absence of an oxidizing zone in the discharge area. Influx of reducing waters results in reducing conditions to the land surface.

presumably been traveling along relatively long flowpaths from the topographically high areas of recharge to the south. There are three wells displaying characteristics of oxidized chemistry (high dissolved oxygen, Figure 33). Each is located in an area likely to be a site of isolated, local recharge. Two are located on flat, sandy areas, while the third is on the top of a hill.

Alkalinity values increase with depth (Figure 35), although the springs would seem apt to have waters with a more reduced chemistry because of their position at the discharge end of a flowpath. The fact that this is an expansive discharge area predicates the existence of flow systems of varying magnitude (Figure 36). Waters from local and intermediate systems should both be discharging in this area. Waters from these two types of flow systems will be evolved to different degrees. Discharge from a local flow system, for example, should have lower alkalinity than water discharging from an intermediate flow system, a result of a relatively short residence time. This results in a mix of chemistries, making it difficult to observe any meaningful trend in alkalinity values.

Relatively long residence times are evident in both springs and deep wells in the till plain. Tritium values from samples LI 0694 01, Lake Alice Spring, and LI 0794 52, Iron Spring, contain no detectable tritium. Samples LI 0794 29R, a 78-foot flowing well, and LI 0794 18R, a 200-foot well, are likewise vintage waters.

CONCLUSIONS

The general configuration of the Itasca moraine and the surrounding landscape as far as geomorphology and hydrology reveals the probable spatial patterns of recharge and discharge in this area. North of the moraine is a till plain of subdued relief with a myriad of springs and flowing wells rich in iron and poor in dissolved oxygen. This is clearly a discharge area. South of the moraine is an outwash plain with little surface water,

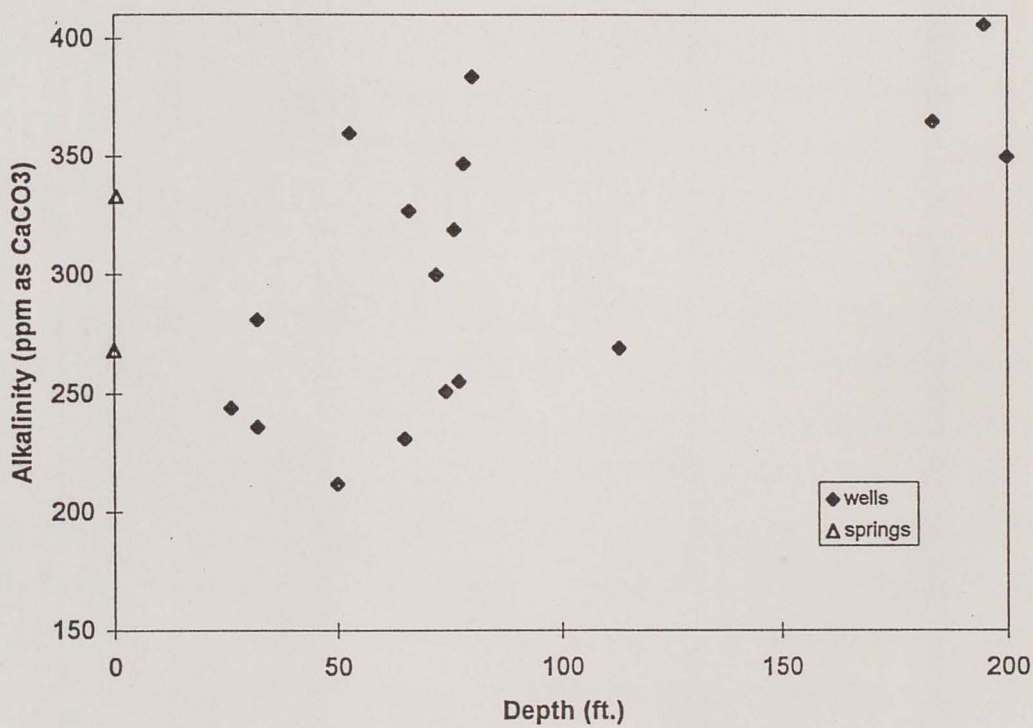


Figure 35. Alkalinity vs. depth in till plain and lacustrine landform assemblages.

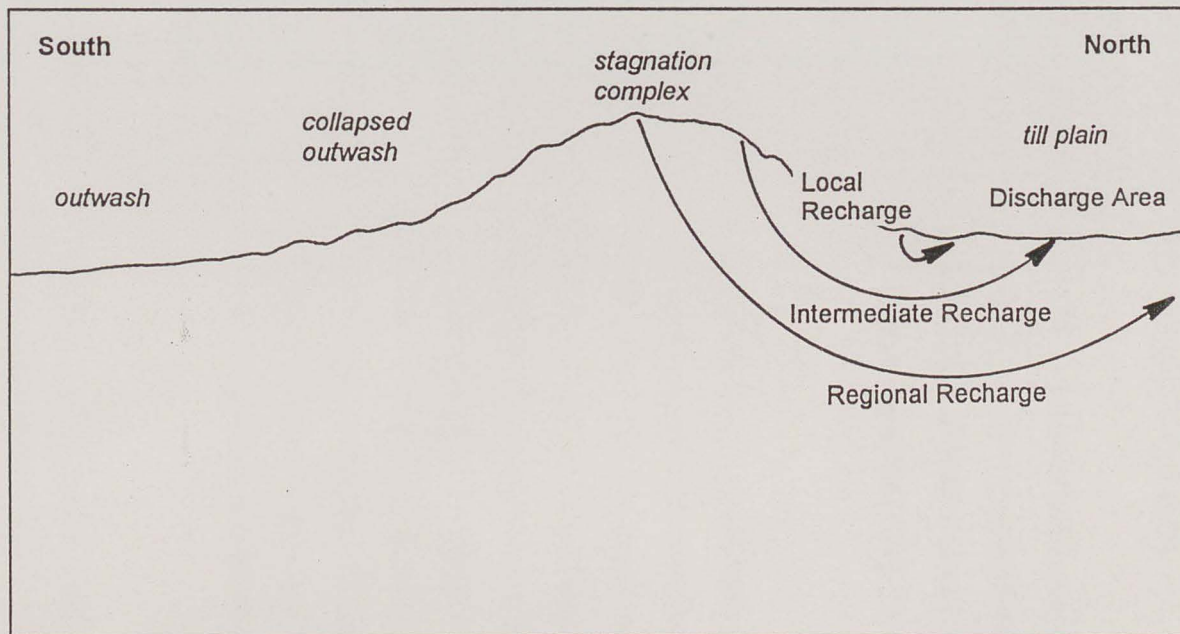


Figure 36. Flow systems of varying magnitude upwelling in a discharge area.

indicating recharge rates are high. The topography of the moraine itself suggests that this, too, may be an area of recharge. In humid regions the water table commonly mimics the land surface, at least on a regional scale (Fetter, 1988). Recharge at topographic highs creates a mound in the water table. The gravitational potential energy drives groundwater flow from topographic highs to lows (Fetter, 1988).

The results of this study show that a geochemical evolution of groundwater takes place between recharge and discharge areas, providing an alternate means for the characterization of groundwater flow. The most notable distinctions between the recharge and discharge waters are a consequence of the redox conditions, the carbonate system, and the isotopic composition.

The redox conditions are very different in areas of recharge versus areas of discharge. In areas with high recharge, oxygenated water infiltrates the upper portions of the aquifer, creating a thick oxidizing zone. The oxidized water is very low in dissolved iron, as most of the iron is in the form of ferric hydroxide. The dissolved oxygen is consumed by oxidation of organic matter during infiltration. When there is no longer any dissolved oxygen remaining, conditions become reducing. Under these conditions ferric hydroxide is no longer stable; it is reduced to ferrous iron. The Eh-pH conditions are within the stability fields of aqueous ferrous iron and siderite. The iron concentration, therefore, is much higher in waters that have crossed the redox boundary. Corollaries to this process are that dissolved oxygen is zero or near zero in the reducing zone, and the redox potential is very low.

The carbonate system affects the groundwater geochemistry by the release of bicarbonate from calcite dissolution and carbonic acid dissociation. There is a large amount of carbonate sediments in the glacial drift. Upon infiltration of precipitation, carbonate

dissolution begins to release calcium and magnesium to solution. Calcium, magnesium, and alkalinity concentrations continue to increase to the point of discharge.

Oxidized waters in this study generally have tritium values indicative of recent recharge, and reduced waters often have no tritium. The absence of detectable tritium in these waters indicates that the time scale involved in the flow system is at least in the order of decades. Some waters have all of the characteristics of a reduced water but also contain tritium. In these cases the flowpath from the recharge point to the discharge point in the reducing zone corresponds to a residence time less than 45 years.

The geomorphic and sedimentologic characteristics of the landforms dictate the potential for recharge over the assemblages. St. George (1994) modeled the groundwater flow over the area using known parameters of aquifer thickness and hydraulic conductivity to estimate recharge. Recharge estimates were assigned to each landform assemblage and were subsequently refined by calibration to the actual water table. The results varied according to both hydraulic conductivity of the aquifer material and the topographic expression of the landform assemblage. The interpretation of groundwater geochemistry is consistent with the landform-based approach of St. George.

Outwash sediments are zones of high recharge. St. George determined values of 15-21 cm/yr. This is consistent with the characteristics of the groundwater sampled in this area. The waters with reduced chemistries come mainly from deep wells, below the redox boundary. Wells producing waters with oxidized chemistries are drawing water from the thick, well-defined oxidizing zone.

Hummocky topography generates numerous local flow systems. These systems discharge to lakes and sloughs within the stagnation complex, resulting in a substantial reduction of recharge to the regional flow system by evaporative pumping. The stagnation complex is

consequently a zone of moderate recharge. St. George determined a rate of 1.2 cm/yr. An oxidizing zone exists in topographically higher portions of the moraine. There are, however, shallow wells or springs producing water with reduced chemistries. These are examples of upward flow from depths below the redox boundary toward discharge areas, a result of local flow systems.

Collapsed outwash sediments have characteristics intermediate between outwash and moraine deposits. There is an oxidizing zone evident from oxygenated water being drawn from shallow depths in this area. There are also shallow waters with reduced chemistries, indicative of discharge from local flow systems. However, because the occurrence of closed depressions within the collapsed outwash is less frequent than in the stagnation complex, there is less opportunity for the development of local flow systems. St. George estimated a recharge rate of 7.6 cm/yr.

The till plain, except for a few local anomalies, is dominated by reduced chemistries. Both shallow and deep wells produce water high in dissolved iron and low in dissolved oxygen, as do the springs. Reducing conditions are present right to the land surface. The absence of an oxidizing zone and the presence of flowing wells and springs indicate that this is a discharge area. Again, these results are consistent with the landform-based approach of St. George; recharge values range from -0.15 to 0.15 cm/yr, effectively zero.

A model of recharge thus emerges. Outwash, collapsed outwash, and stagnation complex landform assemblages contribute recharge to the regional flow system. The collapsed outwash and stagnation complex also contribute to smaller intermediate and local flow systems. Because much of the recharge is tied up in these smaller flow systems, the net recharge to the regional flow system from hummocky landforms is less than the recharge from broad, level outwash landforms. The till plain and lacustrine landform assemblages

discharge groundwater from local and intermediate flow systems. An illustrative summary is shown on Figure 37.

The agreement between the results of this study and the results of St. George indicate that landform-based analysis is a valid approach to the characterization of flow systems in glacial topography.

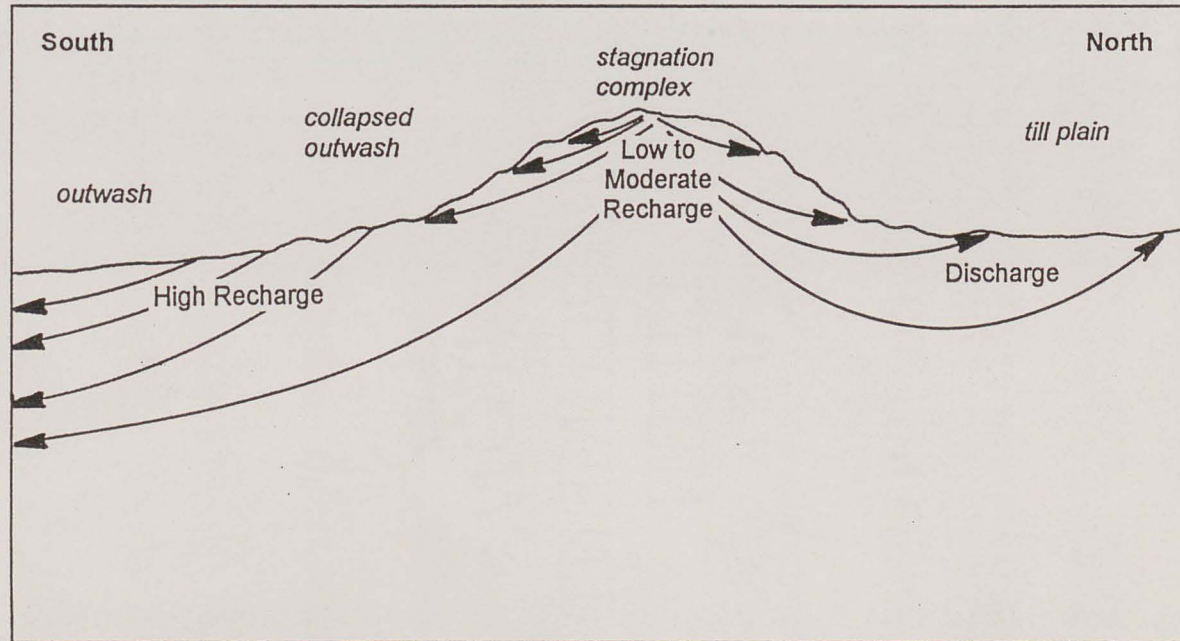


Figure 37. A regional model of recharge. High hydraulic conductivities and level topography are favorable characteristics for high rates of recharge. Hummocky topography provides low to moderate recharge to the intermediate and regional flow systems, as much flow is lost by evaporative pumping from lakes and sloughs within the depressions. Lower-lying areas to the north are zones primarily of discharge.

REFERENCES

- Alexander, S.C. and E.C. Alexander Jr. 1994. Field and Laboratory Methods. Hydrogeochemistry Laboratory, Department of Geology and Geophysics, University of Minnesota (unpublished).
- American Public Health Association (APHA) 1989. Standard Methods for the Examination of Water and Wastewater, 17th Edition. APHA, Washington, D.C.
- Anderson, C.A. 1976. Pleistocene Geology of the Comstock-Sebeka Area, West-Central Minnesota. M.S. Thesis, University of North Dakota.
- Buol, S.W., F.D. Hole, and R.J. McCracken 1973. "Soil Genesis and Classification." The Iowa State University Press, Ames.
- Cardenal, J., J. Benavente, and J.J. Cruz-Sanjulian 1994. Chemical evolution of groundwater in Triassic gypsum-bearing carbonate aquifers (Las Alpujarras, southern Spain). *Journal of Hydrology*, 161: 3-30.
- Domenico, P.A. and F.W. Schwartz 1990. "Physical and Chemical Hydrogeology." John Wiley and Sons, New York.
- Donovan, J.J. and A.W. Rose 1994. Geochemical evolution of lacustrine brines from variable-scale groundwater circulation. *Journal of Hydrology*, 154: 35-62.
- Drever, J.I. 1988. "The Geochemistry of Natural Waters." Prentice Hall, Inc., Englewood Cliffs, NJ.
- Fetter, C.W. 1988. "Applied Hydrogeology." Macmillan Publishing Company, New York.
- Flint, R.F. 1971. "Glacial and Quaternary Geology." John Wiley and Sons, New York.
- Freeze, R.A. and J.A. Cherry 1979. "Groundwater." Prentice Hall, Inc., Englewood Cliffs, NJ.
- Garrels, R.M. and C.L. Christ 1965. "Solutions, Minerals, and Equilibria." Harper & Row, New York.
- Gerla, P.J. 1992. Pathline and geochemical evolution of ground water in a regional discharge area, Red River Valley, North Dakota. *Ground Water*, 30: 743-754.

- Goldstein, B.S. 1985. Stratigraphy, Sedimentology, and Late-Quaternary History of the Wadena Drumlin Region, Central Minnesota. Ph.D. Thesis, University of Minnesota.
- Goldstein, B.S. 1989. Lithology, sedimentology, and genesis of the Wadena drumlin field, Minnesota, USA. *Sedimentary Geology*, 62: 241-277.
- "Goode's World Atlas." 18th ed. 1990. E.B. Espenshade, Jr., ed. Rand McNally, New York.
- Gowan, A. 1993. Sedimentology and Geochemistry of Selected Glacial Sediments from Central Minnesota as a Method for Correlation and Provenance Studies of Glacial Stratigraphic Units. M.S. Thesis, University of Minnesota.
- Harris, K. 1975. Pleistocene Geology of the Grand Forks-Bemidji Area, Northwestern Minnesota. Ph.D. Thesis, University of North Dakota.
- Helgeson, J.O. and G.F. Lindholm 1977. Geology and Water-Supply Potential of the Anoka Sand-Plain Aquifer, Minnesota. Minnesota Department of Natural Resources, Division of Waters, Technical Paper No. 6.
- Hem, J.D. 1989. Study and Interpretation of the Chemical Characteristics of Natural Water. United States Geological Survey Water-Supply Paper 2254.
- Hendry, M.J. and F.W. Schwartz 1990. The chemical evolution of ground water in the Milk River aquifer, Canada. *Ground Water*, 28: 253-261.
- Hobbs, H.C. and J.E. Goebel 1982. Geologic Map of Minnesota: Quaternary Geology. Minnesota Geological Survey, State Map Series, S-1.
- Leverett, F. 1929. Moraines and shore lines of the Lake Superior basin. United States Geological Survey Professional Paper.
- Leverett, F. 1932. Quaternary geology of Minnesota and parts of adjacent states. United States Geological Survey Professional Paper 161.
- Leverett, F. and F.W. Sardeson 1919. Surface formations and agricultural conditions of the south half of Minnesota. Minnesota Geological Survey Bulletin 14.
- Maclay, R.W. and T.C. Winter 1967. Geochemistry and Ground-Water Movement in Northwestern Minnesota. *Ground Water*, 5: 11-19.

- Megard, R.O., J.P. Bradbury, and W.E. Dean 1993. Climatic and limnologic setting of Elk Lake. *in* Elk Lake, Minnesota: Evidence for Rapid Climate Change in the North-Central United States (J.P. Bradbury and W.E. Dean, eds.), pp. 19-36. United States Geological Survey Special Paper 276.
- Meyboom, P. 1966. Unsteady groundwater flow near a willow ring in hummocky moraine. *Journal of Hydrology*, 4: 38-62.
- Meyboom, P. 1967. Mass transfer studies to determine the groundwater regime of permanent lakes in hummocky moraine of western Canada. *Journal of Hydrology*, 5: 117-142.
- Meyer, G. 1993. Surficial Geologic Map of Parts of Koochiching, Itasca, and Beltrami Counties, North-Central Minnesota. University of Minnesota, Minnesota Geological Survey.
- Mooers, H.D. 1988. Quaternary History and Ice Dynamics of the St. Croix Phase of Late Wisconsin Glaciation, Central Minnesota. Ph.D. Thesis, University of Minnesota.
- Mooers, H.D. and P.M. Schulte 1993. A landform-based approach to the estimation of recharge in a complex glacial sedimentary setting. *GSA Abst. Prog.*, v. 25, no. 7.
- Norton, A.R. 1983. Quaternary Geology of the Itasca and St. Croix Moraine Interlobate Area. M.S. Thesis, University of Minnesota.
- Oakes, E.L. and L.E. Bidwell 1968. Water Resources of the Mississippi Headwaters Watershed North-Central Minnesota. United States Geological Survey Hydrologic Investigations Atlas HA-278.
- Palmer, C.D. and J.A. Cherry 1984. Geochemical evolution of groundwater in sequences of sedimentary rocks. *Journal of Hydrology*, 75: 27-65.
- Perkins, R.L. 1977. Late Cenozoic Geology of West-Central Minnesota from Moorhead to Park Rapids. M.S. Thesis, University of North Dakota.
- Rozkowski, A. 1967. The origin of hydrochemical patterns in hummocky moraine. *Canadian Journal of Earth Sciences*, 4: 1065-1092.
- Sackreiter, D. 1975. Quaternary Geology of the Southern Part of the Grand Forks and Bemidji Quadrangles. Ph.D. Thesis, University of North Dakota.
- St. George, L.M. 1994. A Landform-Based Approach to the Estimation of Groundwater Recharge in Complex Glacial Topography. M.S. Thesis, University of Minnesota.

- St. George, L.M. and H.D. Mooers in press. Landform Assemblages and Glacial History of a Portion of the Itasca Moraine, Northcentral Minnesota. Minnesota Geological Survey.
- Siegel, D.I. 1983. Ground water and the evolution of patterned mires, Glacial Lake Agassiz Peatlands, northern Minnesota. *Journal of Ecology*, 71.
- Stark, J.R., D.S. Armstrong, and D.R. Zwilling 1994. Stream-Aquifer Interactions in the Straight River Area, Becker and Hubbard Counties, Minnesota. United States Geological Survey Water-Resources Investigation Report 94-4009.
- Stark, J.R., J.P. Busch, and M.H. Deters 1991. Hydrogeology and Water Quality of Glacial-Drift Aquifers in the Bemidji-Bagley Area, Beltrami, Clearwater, Cass, and Hubbard Counties, Minnesota. United States Geological Survey Water-Resources Investigations Report 89-4136.
- Sugden, D.E. and B.S. John 1976. "Glaciers and Landscapes." Edward Arnold, London.
- Tóth, J. 1963. A theoretical analysis of groundwater flow in small drainage basins. *Journal of Geophysical Research*, 68: 4795-4812.
- Weaver, T.R. and J.M. Bahr 1991a. Geochemical evolution in the Cambrian-Ordovician sandstone aquifer, eastern Wisconsin: 1. Major ion and radionuclide distribution. *Ground Water*, 29: 350-356.
- Weaver, T.R. and J.M. Bahr 1991b. Geochemical evolution in the Cambrian-Ordovician sandstone aquifer, eastern Wisconsin: 2. Correlation between flow paths and ground-water chemistry. *Ground Water*, 29: 510-515.
- Winter, T.C. and R.C. Averett, eds. in press. Interdisciplinary Research Initiative: Hydrologic and Biogeochemical Research in the Shingobee River Headwaters Area, North-Central Minnesota. United States Geological Survey Water-Supply Paper.
- Wolery, T.J. 1992. EQ3NR, a computer program for geochemical aqueous speciation-solubility calculations: theoretical manual, user's guide, and related documentation (Version 7.0). Lawrence Livermore National Laboratory Publication UCRL-MA-110662, pt III.
- Wovcha, D.S. 1989. Lake-Level Change in Relation to Climate in West-Central Minnesota. M.S. Thesis, University of Minnesota.

- Wright, H.E. Jr. 1964. The classification of the Wisconsin Glacial Stage. *Journal of Geology*, 72: 628-637.
- Wright, H.E. Jr. 1972. Quaternary History of Minnesota. *in* "Geology of Minnesota: A Centennial Volume" (P.K. Sims and G.B. Morey, eds.), pp. 515-547. Minnesota Geological Survey, Minneapolis, Minnesota.
- Wright, H.E. Jr. 1993. History of the landscape in the Itasca region. *in* Elk Lake, Minnesota: Evidence for Rapid Climate Change in the North-Central United States (J.P. Bradbury and W.E. Dean, eds.), pp. 7-17. United States Geological Survey Special Paper 276.
- Wright, H.E. Jr. and R.V. Ruhe 1965. Glaciation of Minnesota and Iowa. *in* "The Quaternary of the United States" (H.E. Wright Jr. and D.G. Frey, eds.), pp. 29-41. Princeton University Press, Princeton.
- Zebarth, B.J. and E. DeJong 1989. Water flow in a hummocky landscape in central Saskatchewan, Canada, III. Unsaturated flow in relation to topography and land use. *Journal of Hydrology*, 110: 199-218.

APPENDIX A

Sample data including information from well logs and results of chemical analyses.

Site No.	LI 0894 07 R	LI 0894 10 R	LI 0894 14 R
Site Name	Evenwoll	Bydlon	Clearwater Co. Park
Date	8/12/90	8/9/90	8/9/90
Well Log Data			
MN Unique No.	535396	106416	182883
County	Clearwater	Clearwater	Clearwater
Location	144/36/33ddd	144/36/09bcc	144/37/13cdc
Date Drilled	9/28/89	7/19/73	6/23/84
SWL (ft.)	25 bls	34 bls	15 bls
Screened Interval	44-51 ft.	48-53 ft.	70-77 ft.
Lithology	brown-gray sand	hard yellow sand	soft gray medium sand
pH	7.45	7.28	7.61
meter temp. (°C)	9.7	10.0	11.4
therm temp. (°C)	9.7	9.8	11.0
Conductivity (mS/cm)	0.27	0.46	0.28
temp. (°C)	9.9	10.2	11.4
Redox Potential (mV)	128.2	131.4	-70.1
temp. (°C)	9.7	10	11.4
D.O. (mg/L)			
#1	1.8	5.23	0
#2	1.81	5.14	0.06
mean	1.81	5.19	0.03
std. dev.	0.01	0.06	0.04
Alkalinity (ppm as CaCO₃)			
#1	239	360	254
#2	238	359	254
#3	237	362	256
mean	238	360	255
std. dev.	1.0	1.5	1.2
Isotopes			
³H			
²H			
¹⁸O			
Cations (mg/L)			
Si	6.85	8.76	7.77
Si SD	0.12	0.16	0.14
P	0.12	0.06	0.06
P SD	0.09	0.05	0.04
Mn	0.02	0.01	0.07
Mn SD	0.00	0.00	0.00
Mg	20.05	31.31	21.07
Mg SD	0.34	0.53	0.35
Sr	0.05	0.10	0.09
Sr SD	0.00	0.00	0.00
Al	0.13	0.21	0.14
Al SD	0.01	0.01	0.01

Site No. Site Name (continued)	LI 0894 07 R Evenwoll	LI 0894 10 R Bydlon	LI 0894 14 R Clearwater Co. Park
Fe	0.07	0.06	1.58
Fe SD	0.01	0.02	0.05
K	0.83	5.37	2.51
K SD	0.05	0.16	0.10
Na	1.81	2.97	4.12
Na SD	0.03	0.05	0.07
Ca	65.22	92.01	62.77
Ca SD	1.10	1.54	1.05
Ba	0.04	0.07	0.12
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	1.24	8.65	1.13
NO ₃ (mg N/l)	0.28	4.50	0.02
SO ₄ (mg/l)	8.76	11.69	3.48
Total Hardness	245.24	358.40	243.31
Calculated TDS	240.98	372.70	247.89
Charge Balance			
Cation Sum	5.01	7.44	5.11
Anion Sum	5.00	8.02	5.20
% difference	0.08	-3.75	-0.84

Site No.	LI 0694 15	LI 0694 17	LI 0794 18 R	LI 0894 21 R
Site Name	Katzenmeyer	DeSchane	Olson	Burgoon
Date	6/15/90	6/16/90	7/20/90	8/8/90
Well Log Data				
MN Unique No.		145652	197791	526394
County	Clearwater	Clearwater	Clearwater	Hubbard
Location	144/36/35ad	144/36/03w1/2	145/37/21ddc	145/35/33cdd
Date Drilled	1985	6/28/74	5/29/80	6/22/89
SWL (ft.)		65 bls	58 bls	29 bls
Screened Interval	approx. 80 ft.	107-113 ft.	183-200 ft.	67-72 ft.
Lithology		soft brown sand, gravel	gray sand	soft blue sand
pH	7.07	7.29	7.37	7.29
meter temp. (°C)	9.8	9.0	9.8	10.9
therm temp. (°C)			9.0	10.4
Conductivity (mS/cm)	0.68	0.41	0.51	0.34
temp. (°C)		9.0	9.2	10.9
Redox Potential (mV)	9.1	31	-88.8	-21.9
temp. (°C)	10.7	9	9.4	11.3
D.O. (mg/L)				
#1			0	0
#2			0	0
mean			0.00	0.00
std. dev.			0.00	0.00
Alkalinity (ppm as CaCO₃)				
#1	381	267	347	300
#2	387	269	354	300
#3	384	270	349	301
mean	384	269	350	300
std. dev.	3.0	1.5	3.6	0.6
Isotopes				
³ H			<0.8+/-0.3	
² H			-86.05	
¹⁸ O			-12.11	
Cations (mg/L)				
Si	8.90	8.49	13.83	6.68
Si SD	0.16	0.15	0.25	0.12
P	0.06	0.08	0.20	-0.05
P SD	0.04	0.05	0.17	0.04
Mn	0.34	0.13	0.12	0.15
Mn SD	0.01	0.00	0.00	0.00
Mg	35.19	22.46	30.49	25.17
Mg SD	0.59	0.38	0.51	0.42
Sr	0.13	0.13	0.19	0.09
Sr SD	0.00	0.00	0.00	0.00
Al	0.21	0.14	0.15	0.19
Al SD	0.01	0.01	0.01	0.01

Site No. Site Name (continued)	LI 0694 15 Katzenmeyer	LI 0694 17 DeSchane	LI 0794 18 R Olson	LI 0894 21 R Burgoon
Fe	2.66	1.60	2.27	0.92
Fe SD	0.06	0.04	0.06	0.03
K	2.53	1.99	1.93	1.71
K SD	0.08	0.08	0.07	0.07
Na	4.49	5.27	8.94	4.58
Na SD	0.08	0.09	0.15	0.08
Ca	106.53	69.02	83.78	81.52
Ca SD	1.79	1.16	1.41	1.37
Ba	0.11	0.12	0.15	0.07
Ba SD	0.00	0.00	0.00	0.00
Anions				
Cl (mg/l)	26.97	3.27	0.75	10.62
NO ₃ (mg N/l)	0.07	0.05	0.02	0.13
SO ₄ (mg/l)	35.35	3.84	0.50	6.43
Total Hardness	410.58	264.65	334.45	306.98
Calculated TDS	441.53	267.09	336.40	310.36
Charge Balance				
Cation Sum	8.48	5.58	7.14	6.39
Anion Sum	9.18	5.55	7.03	6.45
% difference	-4.00	0.25	0.72	-0.52

Site No.	I 0894 23	LI 0894 24 R	LI 0694 27	LI 0794 29 R
Site Name	Lucken	Willet	Novack	Periera
Date	8/8/90	8/8/90	6/20/90	7/20/90
Well Log Data				
MN Unique No.	481024	428438	529795	160223
County	Hubbard	Hubbard	Hubbard	Clearwater
Location	44/34/08ad	144/34/32cdc	144/35/25dbb	145/36/15ddc
Date Drilled	4/23/88	6/5/84	12/2/89	11/16/74
SWL (ft.)	15 bls	16 bls	21 bls	11 A(!)ls
Screened Interval	70-74 ft.	28-32 ft.	72-76 ft.	70-78 ft.
Lithology	ard blue sa	gray sand	soft brown sand	fine sand
pH	7.43	7.40	7.15	7.10
meter temp. (°C)	10.9	10.0	11.5	10.1
therm temp. (°C)	10.5	9.9		9.4
Conductivity (mS/cm)	0.28	0.27	0.54	0.61
temp. (°C)	10.8	10.0	11.1	9.4
Redox Potential (mV)	-26.6	259.4	-52	-99.9
temp. (°C)	10.9	10.1	11.6	9.7
D.O. (mg/L)				
#1	0.02	4.94		0
#2	0.02	4.73		0
mean	0.02	4.84		0.00
std. dev.	0.00	0.15		0.00
Alkalinity (ppm as CaCO₃)				
#1	250	239	316	346
#2	251	234	320	349
#3	252	235	320	346
mean	251	236	319	347
std. dev.	1.0	2.6	2.3	1.7
Isotopes				
³ H				<0.8+/-0.3
² H				-69.71
¹⁸ O				-8.80
Cations (mg/L)				
Si	6.37	7.69	10.90	10.25
Si SD	0.11	0.14	0.20	0.18
P	0.02	0.09	0.28	-0.01
P SD	0.03	0.03	0.29	0.04
Mn	0.08	0.01	0.39	0.51
Mn SD	0.00	0.00	0.01	0.01
Mg	20.13	19.24	23.66	28.22
Mg SD	0.34	0.32	0.40	0.47
Sr	0.10	0.08	0.11	0.15
Sr SD	0.00	0.00	0.00	0.00
Al	0.14	0.16	0.20	0.21
Al SD	0.00	0.01	0.01	0.01

Site No. Site Name (continued)	I 0894 23 Lucken	LI 0894 24 R Willet	LI 0694 27 Novack	LI 0794 29 R Periera
Fe	1.09	0.08	10.08	2.98
Fe SD	0.03	0.02	0.20	0.07
K	1.86	1.13	1.67	2.68
K SD	0.07	0.06	0.07	0.10
Na	3.69	2.69	6.12	3.51
Na SD	0.07	0.05	0.11	0.06
Ca	61.74	64.63	87.06	84.42
Ca SD	1.04	1.09	1.46	1.42
Ba	0.04	0.03	0.14	0.24
Ba SD	0.00	0.00	0.00	0.00
Anions				
Cl (mg/l)	1.12	0.68	1.22	0.47
NO ₃ (mg N/l)	0.00	0.48	0.01	0.01
SO ₄ (mg/l)	3.00	4.55	0.20	0.23
Total Hardness	236.89	240.47	314.67	326.77
Calculated TDS	242.14	235.00	311.16	327.75
Charge Balance				
Cation Sum	4.95	4.96	6.61	6.76
Anion Sum	5.11	4.87	6.42	6.96
% difference	-1.65	0.88	1.46	-1.44

Site No.	LI 0694 30	LI 0694 34	LI 0694 35
Site Name	Huschle	Jacobson	Botz
Date	6/21/90	6/27/90	6/27/90
Well Log Data			
MN Unique No.	521561	524864	407686
County	Clearwater	Hubbard	Hubbard
Location	144/37/10dcc	144/35/02aaa	142/35/07ccb
Date Drilled	12/2/88	8/27/89	4/16/82
SWL (ft.)	35 bls	40 bls	7 bls
Screened Interval	184 ft.	62-66 ft.	60-68 ft.
Lithology	soft gray, black sand	sand	soft fine gray sand
pH	7.45	7.37	7.68
meter temp. (°C)	10.9	10.6	12.8
therm temp. (°C)			
Conductivity (mS/cm)	0.55	0.50	0.45
temp. (°C)	11.1	10.4	12.8
Redox Potential (mV)	-46.1	186.7	-72.7
temp. (°C)	11.1		12.6
D.O. (mg/L)			
#1			
#2			
mean			
std. dev.			
Alkalinity (ppm as CaCO₃)			
#1	366	326	282
#2	360	327	282
#3	368	327	281
mean	365	327	282
std. dev.	4.2	0.6	0.6
Isotopes			
³ H			
² H			
¹⁸ O			
Cations (mg/L)			
Si	9.88	7.52	8.03
Si SD	0.18	0.14	0.15
P	0.08	0.13	0.05
P SD	0.04	0.04	0.05
Mn	0.21	0.03	0.16
Mn SD	0.01	0.00	0.00
Mg	31.89	26.72	23.11
Mg SD	0.54	0.45	0.39
Sr	0.14	0.09	0.17
Sr SD	0.00	0.00	0.00
Al	0.15	0.19	0.15
Al SD	0.01	0.01	0.01

Site No. Site Name (continued)	LI 0694 30 Huschle	LI 0694 34 Jacobson	LI 0694 35 Botz
Fe	3.20	1.12	3.21
Fe SD	0.07	0.03	0.07
K	2.48	1.53	1.88
K SD	0.08	0.06	0.08
Na	5.20	4.18	8.54
Na SD	0.09	0.07	0.15
Ca	85.15	91.10	67.04
Ca SD	1.43	1.53	1.13
Ba	0.16	0.05	0.11
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	2.19	3.57	1.31
NO ₃ (mg N/l)	0.04	1.61	0.05
SO ₄ (mg/l)	3.41	5.81	0.66
Total Hardness	343.63	337.29	262.33
Calculated TDS	349.15	330.51	271.59
Charge Balance			
Cation Sum	7.17	6.97	5.67
Anion Sum	7.43	6.87	5.69
% difference	-1.78	0.70	-0.15

Site No.	LI 0694 39	LI 0694 43	LI 0894 101
Site Name	Keller	Goplen	113 Rest Area
Date	6/28/90	6/29/90	8/11/90
Well Log Data			
MN Unique No.	475340	490976	222187
County	Hubbard	Hubbard	Becker
Location	142/35/22bcb	142/34/29ddc	142/37/04bdb
Date Drilled	9/9/87	6/20/87	5/21/67
SWL (ft.)	64 bls	38 bls	12 bls
Screened Interval	91-95 ft.	71-75 ft.	156 ft.
Lithology	medium brown sand and gravel		soft brown water sand
pH	7.30	7.64	7.42
meter temp. (°C)	9.0	9.6	9.8
therm temp. (°C)	8.4	9.2	9.7
Conductivity (mS/cm)	0.43	0.33	0.35
temp. (°C)	8.5	9.2	10.1
Redox Potential (mV)	88.5	114.7	-112.8
temp. (°C)	8.9	9.4	10.5
D.O. (mg/L)			
#1			
#2			
mean			
std. dev.			
Alkalinity (ppm as CaCO ₃)			
#1	294	217	305
#2	298	215	308
#3	296	217	302
mean	296	216	305
std. dev.	2.0	1.2	3.0
Isotopes			
³ H			
² H			
¹⁸ O			
Cations (mg/L)			
Si	7.51	7.77	8.25
Si SD	0.14	0.14	0.15
P	0.03	0.09	0.02
P SD	0.04	0.03	0.03
Mn	0.25	0.15	0.29
Mn SD	0.01	0.00	0.01
Mg	25.74	19.65	23.49
Mg SD	0.43	0.33	0.39
Sr	0.08	0.08	0.09
Sr SD	0.00	0.00	0.00
Al	0.17	0.16	0.18
Al SD	0.01	0.01	0.01

Site No. Site Name (continued)	LI 0694 39 Keller	LI 0694 43 Goplen	LI 0894 101 113 Rest Area
Fe	1.02	2.02	7.04
Fe SD	0.03	0.05	0.14
K	2.05	1.88	3.65
K SD	0.07	0.08	0.13
Na	3.54	3.80	3.21
Na SD	0.06	0.07	0.06
Ca	70.99	60.21	78.12
Ca SD	1.19	1.01	1.31
Ba	0.06	0.09	0.08
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	2.06	2.46	3.90
NO ₃ (mg N/l)	0.11	0.03	0.07
SO ₄ (mg/l)	9.06	11.37	0.05
Total Hardness	283.02	231.10	291.60
Calculated TDS	291.16	229.21	295.48
Charge Balance			
Cation Sum	5.87	4.84	6.07
Anion Sum	6.18	4.64	6.22
% difference	-2.54	2.12	-1.22

Site No.	LI 0894 36 R	LI 0894 37 R
Site Name	Hafics	Carter
Date	8/8/90	8/9/90
Well Log Data		
MN Unique No.	405618	425664
County	Hubbard	Clearwater
Location	142/35/08bcb	145/37/34c
Date Drilled	10/24/80	9/28/82
SWL (ft.)	34 bls	55 bls
Screened Interval	65-69 ft.	191-195 ft.
Lithology	med. brown sand and gravel	gray sand
pH	7.50	7.51
meter temp. (°C)	10.0	11.3
therm temp. (°C)	9.8	10.7
Conductivity (mS/cm)	0.27	0.44
temp. (°C)	10.1	11.3
Redox Potential (mV)	211.5	20.3
temp. (°C)	10	11.7
D.O. (mg/L)		
#1	0.55	0
#2	0.49	0
mean	0.52	0.00
std. dev.	0.04	0.00
Alkalinity (ppm as CaCO ₃)		
#1	236	404
#2	238	410
#3	235	403
mean	236	406
std. dev.	1.5	3.8
Isotopes		
³ H		
² H		
¹⁸ O		
Cations (mg/L)		
Si	7.23	8.18
Si SD	0.13	0.15
P	0.06	0.13
P SD	0.05	0.05
Mn	0.11	0.42
Mn SD	0.00	0.01
Mg	19.13	32.70
Mg SD	0.32	0.55
Sr	0.09	0.31
Sr SD	0.00	0.01
Al	0.16	0.19
Al SD	0.01	0.01

Site No.	LI 0894 36 R	LI 0894 37 R
Site Name	Hafics	Carter
(continued)		
Fe	0.09	0.67
Fe SD	0.02	0.03
K	1.94	2.05
K SD	0.08	0.09
Na	6.15	8.77
Na SD	0.11	0.15
Ca	64.70	90.99
Ca SD	1.09	1.53
Ba	0.11	0.20
Ba SD	0.00	0.00
Anions		
Cl (mg/l)	12.46	1.42
NO ₃ (mg N/l)	0.08	0.04
SO ₄ (mg/l)	2.71	0.31
Total Hardness	240.17	361.55
Calculated TDS	248.97	379.68
Charge Balance		
Cation Sum	5.12	7.68
Anion Sum	5.14	8.16
% difference	-0.18	-3.07

Site No.	LI 0894 42 R	LI 0894 45 R	LI 0794 48R
Site Name	Leistikow	Lowrie	Snyder
Date	8/8/90	8/16/90	7/20/90
Well Log Data			
MN Unique No.	167643	472891	
County	Hubbard	Hubbard	Hubbard
Location	142/34/32baa	143/34/05db	141/35/22dbb
Date Drilled	4/21/77	1991	8/30/86
SWL (ft.)	31 bls	19 bls	9 bls
Screened Interval	72-76 ft.	23-26 ft.	21-26 ft.
Lithology	gray sand	coarse sand	soft brown sand
pH	7.50	7.23	7.45
meter temp. (°C)	9.9	11.2	10.5
therm temp. (°C)	9.4	10.9	9.3
Conductivity (mS/cm)	0.28	0.30	0.71
temp. (°C)	9.9	11.2	9.3
Redox Potential (mV)	72.7	155	-70.3
temp. (°C)	9.9	11.4	
D.O. (mg/L)			
#1	0.05	0.64	0.09
#2	0.03	0.61	0.06
mean	0.04	0.63	0.08
std. dev.	0.01	0.02	0.02
Alkalinity (ppm as CaCO₃)			
#1	233	244	259
#2	235	243	252
#3	235	246	253
mean	234	244	255
std. dev.	1.2	1.5	3.8
Isotopes			
³ H			9.0+/-0.7
² H			-78.18
¹⁸ O			-11.13
Cations (mg/L)			
Si	6.65	7.49	8.79
Si SD	0.12	0.13	0.16
P	0.07	0.03	0.08
P SD	0.04	0.02	0.03
Mn	0.19	0.06	0.16
Mn SD	0.01	0.00	0.00
Mg	18.32	19.89	26.63
Mg SD	0.31	0.34	0.45
Sr	0.06	0.09	0.15
Sr SD	0.00	0.00	0.00
Al	0.21	0.13	0.21
Al SD	0.01	0.01	0.01

Site No.	LI 0894 42 R	LI 0894 45 R	LI 0794 48R
Site Name	Leistikow	Lowrie	Snyder
(continued)			
Fe	1.70	0.22	3.23
Fe SD	0.05	0.01	0.07
K	2.14	1.49	1.48
K SD	0.10	0.06	0.07
Na	2.71	4.08	7.71
Na SD	0.05	0.07	0.13
Ca	63.37	64.31	97.27
Ca SD	1.07	1.08	1.63
Ba	0.12	0.05	0.11
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	1.36	1.65	63.50
NO ₃ (mg N/l)	0.03	0.09	0.62
SO ₄ (mg/l)	6.26	2.37	4.25
Total Hardness	233.55	242.32	352.37
Calculated TDS	234.80	240.47	354.27
Charge Balance			
Cation Sum	4.85	5.06	7.42
Anion Sum	4.86	4.99	7.02
% difference	-0.16	0.74	2.79

Site No.	LI 0894 49 R	LI 0794 50	LI 0794 51	LI 0794 53
Site Name	Kovacovich	Finney	Krause	Guinn #1
Date	8/8/90	7/4/90	7/4/90	7/11/90
Well Log Data				
MN Unique No.	480050	189837	468685	
County	Hubbard	Hubbard	Hubbard	Hubbard
Location	141/35/29aca	141/35/15dba	141/35/20bdc	140/34/29dc
Date Drilled	5/4/88	6/13/80	10/22/86	
SWL (ft.)	20 bls	10 bls	11 bls	
Screened Interval	44 ft.	36-40 ft.	34-39 ft.	approx. 55 ft.
Lithology	soft brown sand	soft sand	soft sand	
pH	6.86	7.50	7.46	7.72
meter temp. (°C)	11.4	11.7	11.5	10.5
therm temp. (°C)	11.1	11.4	10.6	9.6
Conductivity (mS/cm)	0.38	0.47	0.44	0.34
temp. (°C)	11.2	11.4	10.6	9.5
Redox Potential (mV)	-41.8	-97	-33.5	180.4
temp. (°C)	11.1	11.9	11.3	10.1
D.O. (mg/L)				
#1	0	0	0	8.38
#2	0	0	0	8.28
mean	0.00	0.00	0.00	8.33
std. dev.	0.00	0.00	0.00	0.07
Alkalinity (ppm as CaCO₃)				
#1	340	298	282	219
#2	336	302	283	226
#3	333	300	281	224
mean	336	300	282	223
std. dev.	3.5	2.0	1.0	3.6
Isotopes				
³ H				
² H				
¹⁸ O				
Cations (mg/L)				
Si	8.41	10.89	9.18	6.17
Si SD	0.15	0.20	0.17	0.11
P	0.10	0.17	0.07	0.33
P SD	0.05	0.09	0.04	0.81
Mn	0.37	0.16	0.26	0.01
Mn SD	0.01	0.01	0.01	0.00
Mg	23.74	22.38	21.83	17.74
Mg SD	0.40	0.38	0.37	0.30
Sr	0.13	0.14	0.12	0.06
Sr SD	0.00	0.00	0.00	0.00
Al	0.21	0.14	0.19	0.13
Al SD	0.01	0.01	0.01	0.01

Site No.	LI 0894 49 R	LI 0794 50	LI 0794 51	LI 0794 53
Site Name	Kovacovich	Finney	Krause	Guinn #1
(continued)				
Fe	5.24	8.13	3.76	0.00
Fe SD	0.11	0.16	0.08	0.02
K	1.60	2.19	1.22	0.84
K SD	0.08	0.07	0.07	0.05
Na	3.91	4.63	4.20	2.97
Na SD	0.07	0.08	0.07	0.05
Ca	87.52	74.47	73.80	66.55
Ca SD	1.47	1.25	1.24	1.12
Ba	0.12	0.26	0.10	0.04
Ba SD	0.00	0.01	0.00	0.00
Anions				
Cl (mg/l)	0.96	1.64	2.73	3.54
NO ₃ (mg N/l)	0.00	0.05	0.03	2.34
SO ₄ (mg/l)	0.09	0.65	0.31	6.01
Total Hardness	316.13	277.94	274.01	239.12
Calculated TDS	319.62	286.00	273.32	233.79
Charge Balance				
Cation Sum	6.54	5.82	5.70	4.93
Anion Sum	6.76	6.06	5.73	4.85
% difference	-1.66	-2.03	-0.26	0.82

Site No.	LI 0794 54	LI 0794 55	LI 0794 56
Site Name	Guinn #2	Burlingame	Louks
Date	7/11/90	7/11/90	7/11/90
Well Log Data			
MN Unique No.		484195	517587
County	Hubbard	Hubbard	Hubbard
Location	140/34/29dc	141/34/17dba	141/35/27dd
Date Drilled	9/21/89	10/21/88	9/21/88
SWL (ft.)	25 bls	16 bls	10 bls
Screened Interval	51-55 ft.	87-94 ft.	68 ft.
Lithology	soft brown sand	fine gray sand	soft coarse sand (gray)
pH	7.69	7.72	7.68
meter temp. (°C)	9.6	9.2	10.5
therm temp. (°C)	9.0	8.6	10.0
Conductivity (mS/cm)	0.37	0.35	0.31
temp. (°C)	9.0	8.3	9.8
Redox Potential (mV)	-153.8	-64.2	-48.7
temp. (°C)	9.7	9.5	10.7
D.O. (mg/L)			
#1	0	0	0
#2	0	0	0
mean	0.00	0.00	0.00
std. dev.	0.00	0.00	0.00
Alkalinity (ppm as CaCO ₃)			
#1	246	244	197
#2	245	245	204
#3	247	246	205
mean	246	245	202
std. dev.	1.0	1.0	4.4
Isotopes			
³ H			
² H			
¹⁸ O			
Cations (mg/L)			
Si	7.35	8.38	7.73
Si SD	0.13	0.15	0.14
P	0.13	0.15	0.01
P SD	0.04	0.05	0.12
Mn	0.23	0.16	0.13
Mn SD	0.01	0.00	0.00
Mg	20.73	18.65	14.39
Mg SD	0.35	0.31	0.24
Sr	0.10	0.08	0.05
Sr SD	0.00	0.00	0.00
Al	0.19	0.16	0.14
Al SD	0.01	0.01	0.01

Site No.	LI 0794 54	LI 0794 55	LI 0794 56
Site Name	Guinn #2	Burlingame	Louks
(continued)			
Fe	4.59	1.94	1.42
Fe SD	0.10	0.04	0.04
K	1.53	1.67	0.70
K SD	0.07	0.06	0.06
Na	5.06	3.71	3.07
Na SD	0.09	0.06	0.06
Ca	62.65	63.05	60.54
Ca SD	1.05	1.06	1.02
Ba	0.11	0.08	0.04
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	2.16	3.16	2.18
NO ₃ (mg N/l)	0.08	0.08	0.01
SO ₄ (mg/l)	0.55	3.99	6.58
Total Hardness	241.62	234.10	210.35
Calculated TDS	240.34	241.30	208.68
Charge Balance			
Cation Sum	5.10	4.89	4.36
Anion Sum	5.00	5.08	4.24
% difference	0.94	-1.92	1.37

Site No.	LI 0794 58	LI 0794 59	LI 0794 61
Site Name	Steele	Harrison	Lokensgard
Date	7/12/90	7/12/90	7/12/90
Well Log Data			
MN Unique No.	525126	534911	412754
County	Hubbard	Hubbard	Hubbard
Location	140/35/04dcc	140/35/11bcb	140/34/17bad
Date Drilled	6/6/89	8/19/89	11/3/86
SWL (ft.)	22 bls	22 bls	30 bls
Screened Interval	50-54 ft.	64-68 ft.	50-54 ft.
Lithology	soft gray sand	soft gray sand	medium tan sand and cobbles
pH	7.64	7.36	7.40
meter temp. (°C)	9.1	10.6	9.8
therm temp. (°C)	8.9	10.7	9.3
Conductivity (mS/cm)	0.34	0.39	0.34
temp. (°C)	8.6	10.3	9.5
Redox Potential (mV)	-102.6	-104.4	259.6
temp. (°C)	9.4	10.8	9.5
D.O. (mg/L)			
#1	0	0	6.35
#2	0	0	6.26
mean	0.00	0.00	6.31
std. dev.	0.00	0.00	0.06
Alkalinity (ppm as CaCO₃)			
#1	237	249	239
#2	240	248	240
#3	235	247	240
mean	237	248	240
std. dev.	2.5	1.0	0.6
Isotopes			
³ H			
² H			
¹⁸ O			
Cations (mg/L)			
Si	7.62	9.35	7.26
Si SD	0.14	0.17	0.13
P	0.37	0.09	0.04
P SD	0.18	0.02	0.02
Mn	0.19	0.25	0.01
Mn SD	0.01	0.01	0.00
Mg	17.26	17.45	18.94
Mg SD	0.29	0.29	0.32
Sr	0.07	0.09	0.06
Sr SD	0.00	0.00	0.00
Al	0.16	0.16	0.18
Al SD	0.01	0.01	0.01

Site No. Site Name (continued)	LI 0794 58 Steele	LI 0794 59 Harrison	LI 0794 61 Lokensgard
Fe	3.08	8.98	0.00
Fe SD	0.07	0.18	0.01
K	1.40	1.33	1.21
K SD	0.06	0.07	0.06
Na	3.34	3.54	2.02
Na SD	0.06	0.06	0.04
Ca	63.39	66.85	68.58
Ca SD	1.07	1.12	1.15
Ba	0.08	0.09	0.03
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	2.28	1.02	1.15
NO ₃ (mg N/l)	0.11	0.01	0.62
SO ₄ (mg/l)	3.59	0.13	8.44
Total Hardness	229.22	238.65	249.12
Calculated TDS	233.76	239.12	244.77
Charge Balance			
Cation Sum	4.77	4.96	5.10
Anion Sum	4.90	4.99	5.05
% difference	-1.33	-0.32	0.52

Site No.	LI 0794 62	LI 0794 63	LI 0794 64
Site Name	Northern Pine Lodge	Long	Weaver
Date	7/13/90	7/13/90	7/13/90
Well Log Data			
MN Unique No.		529784	
County	Hubbard	Hubbard	Hubbard
Location	141/35/36cca	140/35/21adc	140/34/08bbb
Date Drilled	1950's	11/18/89	4/18/90
SWL (ft.)		21 bls	70 bls
Screened Interval	approx. 80 ft.	35-39 ft.	92-96 ft.
Lithology		soft brown sand	hard brown water sand
pH	7.54	7.49	7.76
meter temp. (°C)	16.5	13.4	9.9
therm temp. (°C)	16.4	13.2	10.0
Conductivity (mS/cm)	0.31	0.43	0.37
temp. (°C)	16.4	13.3	10.2
Redox Potential (mV)	74.9	-32.7	255
temp. (°C)	16.4	13.4	10.6
D.O. (mg/L)			
#1	0.15	0	7.95
#2	0.06	0.05	7.94
mean	0.11	0.03	7.95
std. dev.	0.06	0.04	0.01
Alkalinity (ppm as CaCO ₃)			
#1	182	271	225
#2	185	267	224
#3	184	265	227
mean	184	268	225
std. dev.	1.5	3.1	1.5
Isotopes			
³ H			
² H		-76.29	
¹⁸ O		-11.02	
Cations (mg/L)			
Si	7.99	4.94	6.48
Si SD	0.15	0.09	0.12
P	0.10	0.05	0.02
P SD	0.05	0.04	0.02
Mn	0.16	0.24	0.01
Mn SD	0.00	0.01	0.00
Mg	12.62	22.62	18.61
Mg SD	0.21	0.38	0.31
Sr	0.07	0.06	0.06
Sr SD	0.00	0.00	0.00
Al	0.13	0.13	0.14
Al SD	0.01	0.01	0.01

Site No. Site Name (continued)	LI 0794 62 Northern Pine Lodge	LI 0794 63 Long	LI 0794 64 Weaver
Fe	0.70	1.80	0.02
Fe SD	0.03	0.05	0.01
K	1.14	1.37	1.42
K SD	0.05	0.06	0.06
Na	4.50	2.29	2.15
Na SD	0.08	0.04	0.04
Ca	49.27	73.73	61.59
Ca SD	0.83	1.24	1.04
Ba	0.09	0.03	0.04
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	1.00	1.87	1.52
NO ₃ (mg N/l)	0.03	0.07	0.40
SO ₄ (mg/l)	0.22	8.01	10.35
Total Hardness	174.92	277.08	230.28
Calculated TDS	178.98	270.56	231.24
Charge Balance			
Cation Sum	3.73	5.68	4.74
Anion Sum	3.71	5.58	4.80
% difference	0.21	0.88	-0.61

Site No.	LI 0794 65	LI 0794 66	LI 0794 68
Site Name	Straight River Land and Cattle	Vacationaire	Pritchard
Date	7/13/90	7/13/90	7/18/90
Well Log Data			
MN Unique No.	534929	531699	438635
County	Hubbard	Hubbard	Becker
Location	140/35/26ddd	141/35/10ccc	140/36/21dcc
Date Drilled	11/19/89	10/26/89	5/20/84
SWL (ft.)	34 bls	24 bls	30 bls
Screened Interval	50-54 ft.	104-108 ft.	51-55 ft.
Lithology	medium tan sand and cobbles	coarse sand	soft brown sand
pH	7.62	7.63	7.58
meter temp. (°C)	10.7	9.8	11.8
therm temp. (°C)	9.8	9.6	10.6
Conductivity (mS/cm)	0.47	0.49	0.38
temp. (°C)	9.8	10.2	10.6
Redox Potential (mV)	177.9	-125.7	251.4
temp. (°C)	10.8	10.2	11
D.O. (mg/L)			
#1	0.5	0	5.87
#2	0.47	0	5.99
mean	0.49	0.00	5.93
std. dev.	0.02	0.00	0.08
Alkalinity (ppm as CaCO ₃)			
#1	182	322	209
#2	174	309	208
#3	177	314	209
mean	178	315	209
std. dev.	4.0	6.6	0.6
Isotopes			
³ H			
² H			
¹⁸ O			
Cations (mg/L)			
Si	4.20	10.16	6.33
Si SD	0.08	0.18	0.11
P	0.05	0.38	0.01
P SD	0.03	0.27	0.02
Mn	0.10	0.09	0.00
Mn SD	0.00	0.00	0.00
Mg	18.99	25.19	18.50
Mg SD	0.32	0.42	0.31
Sr	0.06	0.19	0.05
Sr SD	0.00	0.00	0.00
Al	0.17	0.17	0.13
Al SD	0.01	0.01	0.00

Site No.	LI 0794 65	LI 0794 66	LI 0794 68
Site Name	Straight River Land and Cattle	Vacationaire	Pritchard
(continued)			
Fe	0.12	7.26	-0.08
Fe SD	0.02	0.15	0.01
K	1.07	2.07	0.88
K SD	0.07	0.08	0.05
Na	3.16	12.06	1.71
Na SD	0.06	0.21	0.03
Ca	67.64	73.90	60.10
Ca SD	1.14	1.24	1.01
Ba	0.09	0.19	0.02
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	15.18	4.88	4.36
NO ₃ (mg N/l)	7.04	0.07	3.00
SO ₄ (mg/l)	7.44	0.86	7.60
Total Hardness	246.94	288.01	226.09
Calculated TDS	227.12	308.03	221.34
Charge Balance			
Cation Sum	5.11	6.35	4.62
Anion Sum	4.64	6.46	4.67
% difference	4.75	-0.91	-0.54

Site No.	LI 0794 69	LI 0794 71	LI 0794 80
Site Name	Swenson	Teigen	Solberg
Date	7/18/90	7/18/90	7/21/90
Well Log Data			
MN Unique No.	480072	199804	471999
County	Becker	Becker	Becker
Location	140/36/07bca	140/37/26bba	140/36/27add
Date Drilled	6/17/88	8/14/79	4/11/87
SWL (ft.)	30 bls	40 bls	22 bls
Screened Interval	54-56 ft.	74-78 ft.	56-60 ft.
Lithology	soft brown water sand	soft brown sand	med. gray sand
pH	7.41	7.18	7.24
meter temp. (°C)	10.5	9.9	11.6
therm temp. (°C)	9.9	8.9	11.0
Conductivity (mS/cm)	0.37	0.43	0.48
temp. (°C)	9.9	8.8	12.0
Redox Potential (mV)	281.6	174.9	-42.9
temp. (°C)	10	10.2	12.2
D.O. (mg/L)			
#1	0.68	1.59	0
#2	0.64	1.4	0
mean	0.66	1.50	0.00
std. dev.	0.03	0.13	0.00
Alkalinity (ppm as CaCO₃)			
#1	229	282	240
#2	228	281	239
#3	229	284	239
mean	229	282	239
std. dev.	0.6	1.5	0.6
Isotopes			
³ H			
² H			
¹⁸ O			
Cations (mg/L)			
Si	5.41	8.81	5.08
Si SD	0.10	0.16	0.09
P	0.07	0.00	0.00
P SD	0.06	0.00	0.05
Mn	0.01	0.04	0.23
Mn SD	0.00	0.00	0.01
Mg	20.48	24.52	19.65
Mg SD	0.34	0.41	0.33
Sr	0.06	0.10	0.06
Sr SD	0.00	0.00	0.00
Al	0.17	0.22	0.12
Al SD	0.01	0.01	0.01

Site No. Site Name (continued)	LI 0794 69 Swenson	LI 0794 71 Teigen	LI 0794 80 Solberg
Fe	0.06	0.35	0.53
Fe SD	0.01	0.02	0.02
K	1.70	1.17	1.97
K SD	0.06	0.05	0.07
Na	2.25	3.74	3.14
Na SD	0.04	0.06	0.05
Ca	62.32	74.69	59.73
Ca SD	1.05	1.25	1.00
Ba	0.03	0.06	0.02
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	0.90	2.27	0.86
NO ₃ (mg N/l)	0.58	0.14	0.02
SO ₄ (mg/l)	5.92	16.33	7.55
Total Hardness	239.75	287.24	229.87
Calculated TDS	231.33	292.25	236.51
Charge Balance			
Cation Sum	4.94	5.94	4.79
Anion Sum	4.77	6.06	4.97
% difference	1.77	-1.03	-1.88

Site No.	LI 0794 81	LI 0794 82	LI 0794 84
Site Name	Munson	Lymburner	Osage First Baptist Church
Date	7/21/90	7/21/90	7/25/90
Well Log Data			
MN Unique No.	438614	454937	470323
County	Becker	Becker	Becker
Location	139/37/04bbb	140/37/03a	140/36/20dcb
Date Drilled	6/27/84	3/7/85	11/15/86
SWL (ft.)	73 bls	21 bls	33 bls
Screened Interval	158-162 ft.	41-45 ft.	51-55 ft.
Lithology	med. gray silty sand	soft brown sand	soft brown sand
pH	6.76/7.42	7.06/7.80	7.29
meter temp. (°C)	17.5/19.0	16.0/17.3	11.5
therm temp. (°C)			11.2
Conductivity (mS/cm)	0.45		0.27
temp. (°C)	13.9		11.7
Redox Potential (mV)	-130.4	104.1	11.6
temp. (°C)	14.3	11.5	10.5
D.O. (mg/L)			
#1	0	5.84	0.09
#2	0	5.8	0.1
mean	0.00	5.82	0.10
std. dev.	0.00	0.03	0.01
Alkalinity (ppm as CaCO ₃)			
#1	360	191	213
#2	356	193	224
#3	357	193	226
mean	358	192	221
std. dev.	2.1	1.2	7.0
Isotopes			
³ H	<0.8+/-0.3		
² H	-83.31		
¹⁸ O	-11.93		
Cations (mg/L)			
Si	10.56	4.98	4.94
Si SD	0.19	0.09	0.09
P	0.79	0.00	0.06
P SD	0.72	0.00	0.05
Mn	0.11	0.00	0.20
Mn SD	0.00	0.00	0.01
Mg	29.46	18.46	19.07
Mg SD	0.50	0.31	0.32
Sr	0.26	0.05	0.07
Sr SD	0.01	0.00	0.00
Al	0.15	0.13	0.14
Al SD	0.01	0.00	0.01

Site No. Site Name (continued)	LI 0794 81 Munson	LI 0794 82 Lymburner	LI 0794 84 Osage First Baptist Church
Fe	6.18	0.06	0.33
Fe SD	0.13	0.01	0.02
K	2.09	1.16	1.83
K SD	0.08	0.05	0.08
Na	9.57	2.09	3.14
Na SD	0.16	0.04	0.06
Ca	89.87	61.62	59.53
Ca SD	1.51	1.03	1.00
Ba	0.17	0.04	0.06
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	0.68	1.97	2.40
NO ₃ (mg N/l)	0.00	5.69	0.22
SO ₄ (mg/l)	0.05	6.02	2.57
Total Hardness	345.48	229.75	227.00
Calculated TDS	346.32	212.42	221.35
Charge Balance			
Cation Sum	7.39	4.72	4.73
Anion Sum	7.17	4.44	4.56
% difference	1.47	3.07	1.80

Site No.	LI 0794 85	LI 0794 87
Site Name	Pachel	Bebensee
Date	7/25/90	7/25/90
Well Log Data		
MN Unique No.	505773	475318
County	Becker	Becker
Location	140/37/04d	142/36/25aaa
Date Drilled	7/18/85	6/12/87
SWL (ft.)	15 bls	57 bls
Screened Interval	55-59 ft.	85-89 ft.
Lithology	soft brown sandy gravel	med. brown sand and gravel
pH	7.37	7.43
meter temp. (°C)	9.8	11.6
therm temp. (°C)	9.7	11.4
Conductivity (mS/cm)	0.35	0.32
temp. (°C)	10.8	12.0
Redox Potential (mV)	-110.9	-116
temp. (°C)	10.4	12
D.O. (mg/L)		
#1	0	0
#2	0	0
mean	0.00	0.00
std. dev.	0.00	0.00
Alkalinity (ppm as CaCO ₃)		
#1	289	238
#2	288	241
#3	287	241
mean	288	240
std. dev.	1.0	1.7
Isotopes		
³ H		
² H		
¹⁸ O		
Cations (mg/L)		
Si	8.83	6.43
Si SD	0.16	0.12
P	-0.02	0.03
P SD	0.04	0.04
Mn	0.19	0.27
Mn SD	0.01	0.01
Mg	24.07	21.55
Mg SD	0.41	0.36
Sr	0.09	0.08
Sr SD	0.00	0.00
Al	0.20	0.16
Al SD	0.01	0.01

Site No.	LI 0794 85	LI 0794 87
Site Name	Pachel	Bebensee
(continued)		
Fe	5.86	1.79
Fe SD	0.12	0.05
K	2.02	2.01
K SD	0.09	0.08
Na	3.64	3.14
Na SD	0.06	0.06
Ca	72.61	66.48
Ca SD	1.22	1.12
Ba	0.10	0.11
Ba SD	0.00	0.00
Anions		
Cl (mg/l)	1.35	3.97
NO ₃ (mg N/l)	0.01	0.05
SO ₄ (mg/l)	0.12	15.80
Total Hardness	280.21	254.56
Calculated TDS	276.62	257.00
Charge Balance		
Cation Sum	5.82	5.28
Anion Sum	5.80	5.25
% difference	0.12	0.34

Site No.	LI 0794 88	LI 0794 89	LI 0894 102	LI 0894 103
Site Name	Kurtti	Holmer	Thielen	Anderson
Date	7/26/90	7/26/90	8/11/90	8/11/90
Well Log Data				
MN Unique No.		475309		
County	Becker	Becker	Becker	Becker
Location	141/37/11ccc	140/36/29dbd	142/37/16bda	141/37/03aa
Date Drilled		4/21/87		
SWL (ft.)		28 bls	als	approx. 11 bls
Screened Interval	approx. 20 ft.--dug	50-54 ft.	approx. 20 ft.	32 ft.
Lithology				
pH	7.88	7.55	7.49	7.21
meter temp. (°C)	9.2	11.3	10.1	9.4
therm temp. (°C)	8.9	10.8	9.9	9.1
Conductivity (mS/cm)	0.29	0.32	0.27	0.32
temp. (°C)	9.0	11.2	10.1	9.3
Redox Potential (mV)	99.9	-119.3	299.5	-80.1
temp. (°C)	9.4	11.5	10.1	10.2
D.O. (mg/L)				
#1	0.4	0	6.87	0
#2	0.3	0	6.73	0
mean	0.35	0.00	6.80	0.00
std. dev.	0.07	0.00	0.10	0.00
Alkalinity (ppm as CaCO ₃)				
#1	225	267	247	280
#2	225	266	247	281
#3	225	264	246	282
mean	225	266	247	281
std. dev.	0.0	1.5	0.6	1.0
Isotopes				
³ H				
² H				
¹⁸ O				
Cations (mg/L)				
Si	4.88	8.31	6.19	8.74
Si SD	0.09	0.15	0.11	0.16
P	-0.04	-0.04	0.06	0.11
P SD	0.04	0.04	0.05	0.06
Mn	0.03	0.18	0.01	0.22
Mn SD	0.00	0.00	0.00	0.01
Mg	22.61	25.55	21.42	22.80
Mg SD	0.38	0.43	0.36	0.38
Sr	0.05	0.12	0.06	0.07
Sr SD	0.00	0.00	0.00	0.00
Al	0.17	0.15	0.14	0.12
Al SD	0.01	0.01	0.01	0.01

Site No. Site Name (continued)	LI 0794 88 Kurtti	LI 0794 89 Holmer	LI 0894 102 Thielen	LI 0894 103 Anderson
Fe	0.15	2.57	0.06	4.78
Fe SD	0.02	0.06	0.02	0.10
K	1.54	2.13	3.46	1.59
K SD	0.07	0.08	0.11	0.06
Na	1.81	5.36	2.13	2.83
Na SD	0.03	0.09	0.04	0.05
Ca	69.45	60.60	61.77	68.22
Ca SD	1.17	1.02	1.04	1.15
Ba	0.02	0.11	0.03	0.09
Ba SD	0.00	0.00	0.00	0.00
Anions				
Cl (mg/l)	3.32	2.04	2.30	1.18
NO ₃ (mg N/l)	3.03	0.01	0.21	0.01
SO ₄ (mg/l)	5.36	0.18	8.68	0.05
Total Hardness	266.34	256.25	242.24	264.01
Calculated TDS	242.12	255.26	247.97	265.28
Charge Balance				
Cation Sum	5.45	5.42	5.03	5.45
Anion Sum	4.92	5.38	5.20	5.65
% difference	5.03	0.39	-1.63	-1.87

Site No.	LI 0894 104	LI 0894 105	LI 0894 106	LI 0894 107
Site Name	Moorhead	Retz	Eischens	Brookside Resort
Date	8/11/90	8/11/90	8/11/90	8/11/90
Well Log Data				
MN Unique No.	422784	118437		484196
County	Becker	Becker	Becker	Becker
Location	142/36/22dcc	141/36/07cab	141/36/03ccc	141/36/13bdb
Date Drilled	4/19/85	9/29/72		7/21/88
SWL (ft.)	36 bls	60 bls		5 bls
Screened Interval	54-62 ft.	159-163 ft.	approx. 110 ft.	66-70 ft.
Lithology				soft gray sand
pH	7.11	7.68	7.38	7.43
meter temp. (°C)	9.0	10.0	13.6	11.5
therm temp. (°C)	8.9	9.8	13.4	10.7
Conductivity (mS/cm)	0.35	0.27	0.29	0.27
temp. (°C)	8.7	9.8	14.5	10.8
Redox Potential (mV)	-97.2	14.8	-112.6	-123.8
temp. (°C)	9.7	10.4	14.8	11.5
D.O. (mg/L)				
#1	0	0	0	0
#2	0	0	0	0
mean	0.00	0.00	0.00	0.00
std. dev.	0.00	0.00	0.00	0.00
Alkalinity (ppm as CaCO ₃)				
#1	311	249	225	224
#2	310	249	225	225
#3	309	248	231	227
mean	310	249	227	225
std. dev.	1.0	0.6	3.5	1.5
Isotopes				
³ H				
² H				
¹⁸ O				
Cations (mg/L)				
Si	9.42	7.79	8.44	7.28
Si SD	0.17	0.14	0.15	0.13
P	0.30	0.03	0.10	0.08
P SD	0.16	0.04	0.05	0.04
Mn	0.32	0.14	0.12	0.33
Mn SD	0.01	0.00	0.00	0.01
Mg	23.33	19.46	21.80	18.75
Mg SD	0.39	0.33	0.37	0.32
Sr	0.10	0.11	0.11	0.08
Sr SD	0.00	0.00	0.00	0.00
Al	0.13	0.14	0.12	0.12
Al SD	0.01	0.01	0.01	0.01

Site No. Site Name (continued)	LI 0894 104 Moorhead	LI 0894 105 Retz	LI 0894 106 Eischens	LI 0894 107 Brookside Resort
Fe	9.34	1.70	1.74	1.63
Fe SD	0.18	0.05	0.05	0.04
K	2.42	1.57	2.82	1.77
K SD	0.08	0.08	0.10	0.07
Na	3.42	6.06	3.90	3.56
Na SD	0.06	0.10	0.07	0.06
Ca	77.82	60.29	50.62	61.75
Ca SD	1.31	1.01	0.85	1.04
Ba	0.10	0.12	0.07	0.10
Ba SD	0.00	0.00	0.00	0.00
Anions				
Cl (mg/l)	2.00	0.98	1.28	0.97
NO ₃ (mg N/l)	0.03	0.01	0.00	0.00
SO ₄ (mg/l)	0.05	0.90	0.05	6.41
Total Hardness	290.22	230.53	215.94	231.24
Calculated TDS	295.07	238.47	216.68	228.40
Charge Balance				
Cation Sum	6.02	4.92	4.57	4.83
Anion Sum	6.26	5.02	4.58	4.67
% difference	-1.96	-1.04	-0.14	1.68

Site No.	LI 0894 108	LI 0894 117	LI 0894 119
Site Name	Schmitz	Geller	Ross
Date	8/11/90	8/16/90	8/16/90
Well Log Data			
MN Unique No.	461517		423226
County	Becker	Hubbard	Clearwater
Location	141/36/13bb	145/35/23ddb	144/36/30ccb
Date Drilled	5/28/86		6/8/83
SWL (ft.)	32 bls		35 bls
Screened Interval	10-60 ft.	approx. 50 ft.	86-90 ft.
Lithology	soft brown sand		soft gray medium sand
pH	7.33	7.56	7.42
meter temp. (°C)	9.8	9.9	11.7
therm temp. (°C)	9.6	8.8	10.0
Conductivity (mS/cm)	0.27	0.24	0.40
temp. (°C)	10.0	9.2	10.8
Redox Potential (mV)	42.7	-151.9	-141.1
temp. (°C)	9.8	9.7	11.1
D.O. (mg/L)			
#1	2.14	0	0
#2	1.99	0	0
mean	2.07	0.00	0.00
std. dev.	0.11	0.00	0.00
Alkalinity (ppm as CaCO ₃)			
#1	211	212	333
#2	212	211	334
#3	212	214	337
mean	212	212	335
std. dev.	0.6	1.5	2.1
Isotopes			
³ H			
² H			
¹⁸ O			
Cations (mg/L)			
Si	4.74	9.83	8.78
Si SD	0.09	0.18	0.16
P	0.06	0.12	0.06
P SD	0.05	0.04	0.04
Mn	0.03	0.14	0.30
Mn SD	0.00	0.00	0.01
Mg	19.76	17.99	26.53
Mg SD	0.33	0.30	0.45
Sr	0.06	0.08	0.11
Sr SD	0.00	0.00	0.00
Al	0.14	0.12	0.18
Al SD	0.01	0.01	0.01

Site No. Site Name (continued)	LI 0894 108 Schmitz	LI 0894 117 Geller	LI 0894 119 Ross
Fe	0.12	1.42	6.01
Fe SD	0.02	0.04	0.13
K	1.37	1.59	2.20
K SD	0.07	0.08	0.09
Na	2.47	5.51	5.86
Na SD	0.04	0.10	0.10
Ca	63.15	55.10	82.34
Ca SD	1.06	0.93	1.38
Ba	0.05	0.07	0.11
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	10.16	2.00	1.15
NO ₃ (mg N/l)	2.60	0.05	0.06
SO ₄ (mg/l)	13.47	3.76	1.03
Total Hardness	238.90	211.52	314.64
Calculated TDS	239.99	213.39	319.98
Charge Balance			
Cation Sum	4.92	4.51	6.61
Anion Sum	4.99	4.39	6.75
% difference	-0.66	1.44	-1.08

Site No.	LI 0894 125	LI 0694 01	LI 0694 04
Site Name	Traun	Lake Alice Spring	Elk Lake Springs
Date	8/17/90	6/15/90	6/8/90
Well Log Data			
MN Unique No.	494780		
County	Hubbard	Hubbard	Clearwater
Location	143/35/05dda	143/35/15adcd	143/36/23bcbc
Date Drilled	7/28/87		
SWL (ft.)	13 bls		
Screened Interval	61-65 ft.		
Lithology	soft gray water sand		
pH	7.47	6.75	7.20
meter temp. (°C)	11.0	6.1	7.0
therm temp. (°C)	10.7		6.5
Conductivity (mS/cm)	0.33	0.41	0.32
temp. (°C)	10.9	5.9	
Redox Potential (mV)	193.4	-35.4	-113.4
temp. (°C)	10.9		
D.O. (mg/L)			
#1	0	0.06	2.84
#2	0	0	2.27
mean	0.00	0.03	2.56
std. dev.	0.00	0.04	0.40
Alkalinity (ppm as CaCO₃)			
#1	230	262	332
#2	234	270	336
#3	230	272	336
mean	231	268	335
std. dev.	2.3	5.3	2.3
Isotopes			
³ H		<0.8+/-0.3	
² H		-76.78	
¹⁸ O		-10.57	
Cations (mg/L)			
Si	7.43	9.07	9.16
Si SD	0.14	0.16	0.16
P	0.08	0.33	0.29
P SD	0.04	0.16	0.11
Mn	0.11	0.25	0.28
Mn SD	0.00	0.01	0.01
Mg	18.47	22.34	24.70
Mg SD	0.31	0.38	0.41
Sr	0.09	0.12	0.11
Sr SD	0.00	0.00	0.00
Al	0.11	0.11	0.25
Al SD	0.01	0.01	0.01

Site No. Site Name (continued)	LI 0894 125 Traun	LI 0694 01 Lake Alice Spring	LI 0694 04 Elk Lake Springs
Fe	1.03	5.51	9.64
Fe SD	0.03	0.11	0.19
K	1.46	1.89	2.44
K SD	0.06	0.07	0.08
Na	3.76	5.38	4.38
Na SD	0.07	0.09	0.08
Ca	61.84	75.91	76.13
Ca SD	1.04	1.28	1.28
Ba	0.08	0.12	0.14
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	1.69	1.36	1.70
NO ₃ (mg N/l)	0.01	0.04	0.62
SO ₄ (mg/l)	7.38	0.64	1.26
Total Hardness	230.31	281.36	291.58
Calculated TDS	233.39	268.35	312.03
Charge Balance			
Cation Sum	4.81	5.91	6.09
Anion Sum	4.83	5.41	6.82
% difference	-0.20	4.41	-5.63

Site No.	LI 0794 52	LI 0794 73	LI 0794 99
Site Name	Iron Springs Bog	Nicollet Spring	Basswood Spring
Date	7/5/90	7/19/90	7/27/90
Well Log Data			
MN Unique No.			
County	Clearwater	Clearwater	Becker
Location	144/36/28cdc	143/36/21dda	142/36/21ccd
Date Drilled			
SWL (ft.)			
Screened Interval			
Lithology			
pH	7.44	7.31	7.63
meter temp. (°C)	9.8	7.4	19.1
therm temp. (°C)	9.2		18.8
Conductivity (mS/cm)	0.53	0.29	0.38
temp. (°C)	9.8	6.9	18.8
Redox Potential (mV)	-63.5	153.5	-37
temp. (°C)	9.6	8.1	19.2
D.O. (mg/L)			
#1	0.36	2.5	3.57
#2	0.33	2.59	3.48
mean	0.35	2.55	3.53
std. dev.	0.02	0.06	0.06
Alkalinity (ppm as CaCO ₃)			
#1	336	212	295
#2	331	209	294
#3	333	209	293
mean	333	210	294
std. dev.	2.5	1.7	1.0
Isotopes			
³ H		27.5+/-1.9	
² H	-79.06	-72.80	
¹⁸ O	-10.52	-9.25	
Cations (mg/L)			
Si	9.48	7.24	10.51
Si SD	0.17	0.13	0.19
P	0.10	0.18	0.06
P SD	0.02	0.15	0.05
Mn	0.20	0.05	0.17
Mn SD	0.01	0.00	0.00
Mg	26.72	18.60	24.09
Mg SD	0.45	0.31	0.41
Sr	0.14	0.07	0.14
Sr SD	0.00	0.00	0.00
Al	0.22	0.15	0.16
Al SD	0.01	0.01	0.01

Site No.	LI 0794 52	LI 0794 73	LI 0794 99
Site Name	Iron Springs Bog	Nicollet Spring	Basswood Spring
(continued)			
Fe	5.80	0.16	1.57
Fe SD	0.12	0.02	0.04
K	2.21	1.45	1.48
K SD	0.09	0.06	0.07
Na	5.85	2.91	4.94
Na SD	0.10	0.05	0.09
Ca	80.38	55.84	71.71
Ca SD	1.35	0.94	1.20
Ba	0.15	0.06	0.13
Ba SD	0.00	0.00	0.00
Anions			
Cl (mg/l)	1.31	0.51	0.29
NO ₃ (mg N/l)	0.07	0.02	0.12
SO ₄ (mg/l)	0.83	0.47	0.00
Total Hardness	310.50	215.86	278.06
Calculated TDS	317.38	205.80	279.03
Charge Balance			
Cation Sum	6.53	4.48	5.82
Anion Sum	6.73	4.23	5.90
% difference	-1.53	2.93	-0.67

Site No.	LI 0894 100
Site Name	Blue Lake Spring
Date	8/10/90
Well Log Data	
MN Unique No.	
County	Hubbard
Location	141/34/16ccb
Date Drilled	
SWL (ft.)	
Screened Interval	
Lithology	
pH	7.11
meter temp. (°C)	
therm temp. (°C)	7.8
Conductivity (mS/cm)	0.23
temp. (°C)	
Redox Potential (mV)	-90
temp. (°C)	
D.O. (mg/L)	
#1	0
#2	0
mean	0.00
std. dev.	0.00
Alkalinity (ppm as CaCO ₃)	
#1	318
#2	317
#3	320
mean	318
std. dev.	1.5
Isotopes	
³ H	
² H	-72.90
¹⁸ O	-9.32
Cations (mg/L)	
Si	9.00
Si SD	0.16
P	-0.04
P SD	0.04
Mn	0.20
Mn SD	0.01
Mg	25.58
Mg SD	0.43
Sr	0.11
Sr SD	0.00
Al	0.19
Al SD	0.01

Site No.
Site Name
(continued)

LI 0894 100
Blue Lake Spring

Fe	3.12
Fe SD	0.07
K	2.09
K SD	0.09
Na	4.26
Na SD	0.07
Ca	75.62
Ca SD	1.27
Ba	0.10
Ba SD	0.00
Anions	
Cl (mg/l)	1.21
NO ₃ (mg N/l)	0.01
SO ₄ (mg/l)	0.10
Total Hardness	293.91
Calculated TDS	299.86
Charge Balance	
Cation Sum	6.12
Anion Sum	6.41
% difference	-2.27

APPENDIX B

Results of duplicates and spikes.

Duplicate cation analyses					
Site No.	Site Name	Si	P	Mn	Mg
LI 0894 10 R	Bydlon	8.76	0.06	0.01	31.31
		8.68	0.06	0.01	31.14
	% error	-0.94	0.00	80.00	-0.56
LI 0894 21 R	Burgoon	6.68	-0.05	0.15	25.17
		6.78	0.07	0.15	24.02
	% error	1.63	-244.02	-2.78	-4.56
LI 0894 24 R	Willet	7.69	0.09	0.01	19.24
		7.34	0.02	0.01	18.69
	% error	-4.53	-81.63	-44.88	-2.88
LI 0694 30	Huschle	9.88	0.08	0.21	31.89
		9.92	0.13	0.21	32.14
	% error	0.39	71.09	-1.37	0.79
LI 0694 43	Goplen	7.77	0.09	0.15	19.65
		7.63	0.04	0.15	19.18
	% error	-1.81	-52.31	-3.70	-2.38
LI 0794 55	Burlingame	8.38	0.15	0.16	18.65
		7.81	0.14	0.16	18.67
	% error	-6.76	-3.71	-1.10	0.07
LI 0794 58	Steele	7.62	0.37	0.19	17.26
		7.79	0.06	0.19	17.92
	% error	2.22	-84.55	0.47	3.87
LI 0794 59	Harrison	9.35	0.09	0.25	17.45
		9.27	0.08	0.24	16.86
	% error	-0.87	-17.05	-2.16	-3.34
LI 0794 63	Long	4.94	0.05	0.24	22.62
		4.87	0.24	0.23	22.18
	% error	-1.49	421.65	-3.50	-1.98
LI 0794 66	Vacationaire	10.16	0.38	0.09	25.19
		10.24	0.13	0.09	25.55
	% error	0.86	-65.73	2.19	1.45
LI 0794 84	Osage First Baptist Church	4.94	0.06	0.20	19.07
		4.72	0.03	0.19	19.25
	% error	-4.48	-41.27	-3.37	0.93
LI 0794 85	Pachel	8.83	-0.02	0.19	24.07
		8.55	0.05	0.19	23.36
	% error	-3.07	-422.37	-3.60	-2.95
LI 0794 88	Kurtti	4.88	-0.04	0.03	22.61
		4.85	0.01	0.03	22.09
	% error	-0.62	-118.33	-5.82	-2.33
LI 0894 103	Anderson	8.74	0.11	0.22	22.80
		8.84	0.12	0.22	23.38
	% error	1.20	7.42	0.72	2.57

Duplicate cation analyses					
Site No.	Site Name	Si	P	Mn	Mg
LI 0894 106	Eischens	8.44	0.10	0.12	21.80
		8.64	0.02	0.12	21.53
	% error	2.39	-76.76	2.28	-1.26
LI 0894 119	Ross	8.78	0.06	0.30	26.53
		8.76	0.00	0.31	27.08
	% error	-0.18	-100.00	3.38	2.05
LI 0694 04	Elk Lake Springs	9.16	0.29	0.28	24.70
		8.60	0.25	0.34	23.74
	% error	-6.16	-12.60	20.63	-3.88
LI 0894 100	Blue Lake Spring	9.00	-0.04	0.20	25.58
		8.77	-0.04	0.20	25.46
	% error	-2.59	0.00	-1.87	-0.45

Duplicate cation analyses					
Site No.	Site Name	Sr	Al	Fe	K
LI 0894 10 R	Bydlon	0.10	0.21	0.06	5.37
		0.10	0.22	0.08	5.31
	% error	-0.82	0.42	20.09	-1.21
LI 0894 21 R	Burgoon	0.09	0.19	0.92	1.71
		0.09	0.15	0.91	1.71
	% error	-3.39	-19.10	-0.47	0.19
LI 0894 24 R	Willet	0.08	0.16	0.08	1.13
		0.08	0.15	0.00	0.99
	% error	-4.34	-5.34	-95.58	-12.49
LI 0694 30	Huschle	0.14	0.15	3.20	2.48
		0.14	0.16	3.13	2.48
	% error	0.51	6.03	-2.09	0.04
LI 0694 43	Goplen	0.08	0.16	2.02	1.88
		0.07	0.15	1.89	1.76
	% error	-7.30	-6.39	-6.77	-6.31
LI 0794 55	Burlingame	0.08	0.16	1.94	1.67
		0.08	0.19	2.03	1.68
	% error	0.71	15.19	4.96	0.98
LI 0794 58	Steele	0.07	0.16	3.08	1.40
		0.07	0.16	2.83	1.24
	% error	0.15	1.47	-8.16	-11.00
LI 0794 59	Harrison	0.09	0.16	8.98	1.33
		0.09	0.16	9.25	1.30
	% error	-0.58	-0.75	2.99	-2.45
LI 0794 63	Long	0.06	0.13	1.80	1.37
		0.06	0.12	1.78	1.33
	% error	-1.70	-6.03	-0.92	-2.93
LI 0794 66	Vacationaire	0.19	0.17	7.26	2.07
		0.19	0.17	7.13	2.30
	% error	0.52	-0.82	-1.82	10.85
LI 0794 84	Osage First Baptist Church	0.07	0.14	0.33	1.83
		0.07	0.14	0.29	1.80
	% error	-0.71	-3.18	-13.18	-1.64
LI 0794 85	Pachel	0.09	0.20	5.86	2.02
		0.09	0.18	5.31	1.74
	% error	-6.31	-6.40	-9.48	-14.04
LI 0794 88	Kurtti	0.05	0.17	0.15	1.54
		0.05	0.14	0.00	1.49
	% error	-4.67	-17.00	-101.16	-3.24
LI 0894 103	Anderson	0.07	0.12	4.78	1.59
		0.07	0.11	4.80	1.48
	% error	1.21	-4.24	0.55	-6.83

Duplicate cation analyses					
Site No.	Site Name	Sr	Al	Fe	K
LI 0894 106	Eischens	0.11	0.12	1.74	2.82
		0.11	0.11	1.83	2.66
	% error	3.04	-7.78	5.61	-5.95
LI 0894 119	Ross	0.11	0.18	6.01	2.20
		0.12	0.18	6.01	2.19
	% error	0.96	0.06	-0.05	-0.63
LI 0694 04	Elk Lake Springs	0.11	0.25	9.64	2.44
		0.10	0.17	10.80	2.15
	% error	-9.83	-33.06	12.03	-12.05
LI 0894 100	Blue Lake Spring	0.11	0.19	3.12	2.09
		0.11	0.18	3.26	2.26
	% error	1.03	-2.24	4.69	8.41

Duplicate cation analyses				
Site No.	Site Name	Na	Ca	Ba
LI 0894 10 R	Bydlon	2.97	92.01	0.07
		3.00	93.63	0.07
	% error	0.78	1.76	3.09
LI 0894 21 R	Burgoon	4.58	81.52	0.07
		4.59	79.54	0.07
	% error	0.25	-2.43	-1.20
LI 0894 24 R	Willet	2.69	64.63	0.03
		2.58	61.69	0.03
	% error	-3.98	-4.56	-12.65
LI 0694 30	Huschle	5.20	85.15	0.16
		5.14	85.00	0.16
	% error	-1.00	-0.18	1.64
LI 0694 43	Goplen	3.80	60.21	0.09
		3.69	57.15	0.08
	% error	-2.71	-5.08	-8.15
LI 0794 55	Burlingame	3.71	63.05	0.08
		3.62	63.39	0.08
	% error	-2.41	0.54	1.68
LI 0794 58	Steele	3.34	63.39	0.08
		3.21	61.31	0.08
	% error	-3.97	-3.28	-1.50
LI 0794 59	Harrison	3.54	66.85	0.09
		3.61	65.52	0.09
	% error	2.05	-1.99	-1.28
LI 0794 63	Long	2.29	73.73	0.03
		2.26	70.97	0.03
	% error	-1.35	-3.74	-5.97
LI 0794 66	Vacationaire	12.06	73.90	0.19
		11.89	75.36	0.20
	% error	-1.44	1.98	2.36
LI 0794 84	Osage First Baptist Church	3.14	59.53	0.06
		3.10	59.45	0.06
	% error	-1.09	-0.14	-0.63
LI 0794 85	Pachel	3.64	72.61	0.10
		3.31	68.59	0.09
	% error	-9.26	-5.54	-6.96
LI 0794 88	Kurtti	1.81	69.45	0.02
		1.77	68.40	0.02
	% error	-1.82	-1.51	-12.39
LI 0894 103	Anderson	2.83	68.22	0.09
		2.86	69.81	0.09
	% error	0.95	2.33	2.81

Duplicate cation analyses				
Site No.	Site Name	Na	Ca	Ba
LI 0894 106	Eischens	3.90	50.62	0.07
		4.08	52.87	0.07
	% error	4.69	4.43	2.37
LI 0894 119	Ross	5.86	82.34	0.11
		5.93	84.20	0.12
	% error	1.19	2.26	2.80
LI 0694 04	Elk Lake Springs	4.38	76.13	0.14
		3.97	80.33	0.15
	% error	-9.33	5.52	6.59
LI 0894 100	Blue Lake Spring	4.26	75.62	0.10
		4.33	77.29	0.11
	% error	1.78	2.21	2.04

Duplicate anion analyses				
Site No.	Site Name	Cl (mg/l)	NO3 (mg N/l)	SO4 (mg/l)
LI 0694 27	Novack	1.22	0.01	0.20
LI 0694 28	duplicate Novack	1.63	0.05	1.00
	% error	33.01	381.82	388.24
LI 0694 30	Huschle	2.19	0.04	3.41
LI 0694 31	duplicate Huschle	2.98	0.06	4.18
	% error	35.89	60.53	22.84
LI 0794 69	Swenson	0.90	0.58	5.92
LI 0794 70	duplicate Swenson	1.64	1.06	10.51
	% error	82.59	82.59	77.55
LI 0894 108	Schmitz	10.16	2.60	13.47
LI 0894 109	duplicate Schmitz	9.75	2.55	12.43
	% error	-4.07	-1.92	-7.70
LI 0894 119	Ross	1.15	0.06	1.03
LI 0894 120	duplicate Ross	0.93	0.02	1.00
	% error	-18.52	-62.90	-3.29
LI 0894 125	Traun	1.69	0.01	7.38
LI 0894 126	duplicate Traun	1.65	0.01	7.38
	% error	-1.96	42.86	0.07

Samples spiked with 2 ppm Fe							
Site No.	Site Name	Si	P	Mn	Mg	Sr	Al
LI 0894 07 R	Evenwoll	6.85	0.12	0.02	20.05	0.05	0.13
	spike	6.89	0.03	0.02	20.59	0.05	0.11
	% error	0.61	-72.53	-8.28	2.70	-2.23	-12.04
LI 0794 18 R	Olson	13.83	0.20	0.12	30.49	0.19	0.15
	spike	12.69	0.19	0.12	29.94	0.18	0.18
	% error	-8.27	-2.56	-0.26	-1.81	-9.47	24.85
LI 0794 53	Guinn #1	6.17	0.33	0.01	17.74	0.06	0.13
	spike	6.51	0.02	0.00	18.17	0.06	0.13
	% error	5.38	-92.57	-60.81	2.40	1.96	-3.25
LI 0794 55	Burlingame	8.38	0.15	0.16	18.65	0.08	0.16
	spike	8.16	0.20	0.16	18.02	0.08	0.14
	% error	-2.55	35.63	-2.20	-3.39	-4.16	-14.03
LI 0794 58	Steele	7.62	0.37	0.19	17.26	0.07	0.16
	spike	7.41	0.04	0.21	18.12	0.07	0.17
	% error	-2.76	-87.84	8.15	5.01	2.91	10.20
LI 0794 69	Swenson	5.41	0.07	0.01	20.48	0.06	0.17
	spike	5.18	0.16	0.00	19.68	0.06	0.17
	% error	-4.26	134.83	-66.36	-3.90	-2.41	-2.32
LI 0794 80	Solberg	5.08	0.00	0.23	19.65	0.06	0.12
	spike	5.12	-0.02	0.22	19.54	0.06	0.12
	% error	0.74	-900.00	-3.82	-0.56	-5.16	-4.31
LI 0894 104	Moorhead	9.42	0.30	0.32	23.33	0.10	0.13
	spike	9.47	0.03	0.32	23.85	0.10	0.18
	% error	0.49	-90.74	-1.70	2.19	2.53	38.71

Samples spiked with 2 ppm Fe						
Site No.	Site Name	Fe	K	Na	Ca	Ba
LI 0894 07 R	Evenwoll	0.07	0.83	1.81	65.22	0.04
	spike	1.95	0.80	1.73	64.32	0.04
	% error	-5.65	-3.31	-4.36	-1.38	-2.67
LI 0794 18 R	Olson	2.27	1.93	8.94	83.78	0.15
	spike	4.15	1.85	7.80	76.58	0.14
	% error	-2.81	-4.43	-12.80	-8.59	-5.91
LI 0794 53	Guinn #1	0.00	0.84	2.97	66.55	0.04
	spike	2.05	0.90	3.11	69.95	0.04
	% error	2.22	6.15	4.68	5.11	8.78
LI 0794 55	Burlingame	1.94	1.67	3.71	63.05	0.08
	spike	4.01	1.62	3.47	61.88	0.08
	% error	1.82	-3.03	-6.49	-1.86	-4.92
LI 0794 58	Steele	3.08	1.40	3.34	63.39	0.08
	spike	5.24	1.31	3.29	63.84	0.08
	% error	3.03	-6.39	-1.73	0.71	2.88
LI 0794 69	Swenson	0.06	1.70	2.25	62.32	0.03
	spike	1.99	1.71	2.29	61.68	0.03
	% error	-3.41	1.04	2.04	-1.01	-4.76
LI 0794 80	Solberg	0.53	1.97	3.14	59.73	0.02
	spike	2.60	1.80	3.17	59.96	0.02
	% error	2.80	-8.92	0.91	0.40	-13.33
LI 0894 104	Moorhead	9.34	2.42	3.42	77.82	0.10
	spike	12.24	2.55	3.39	78.97	0.10
	% error	7.97	5.24	-0.75	1.48	2.51